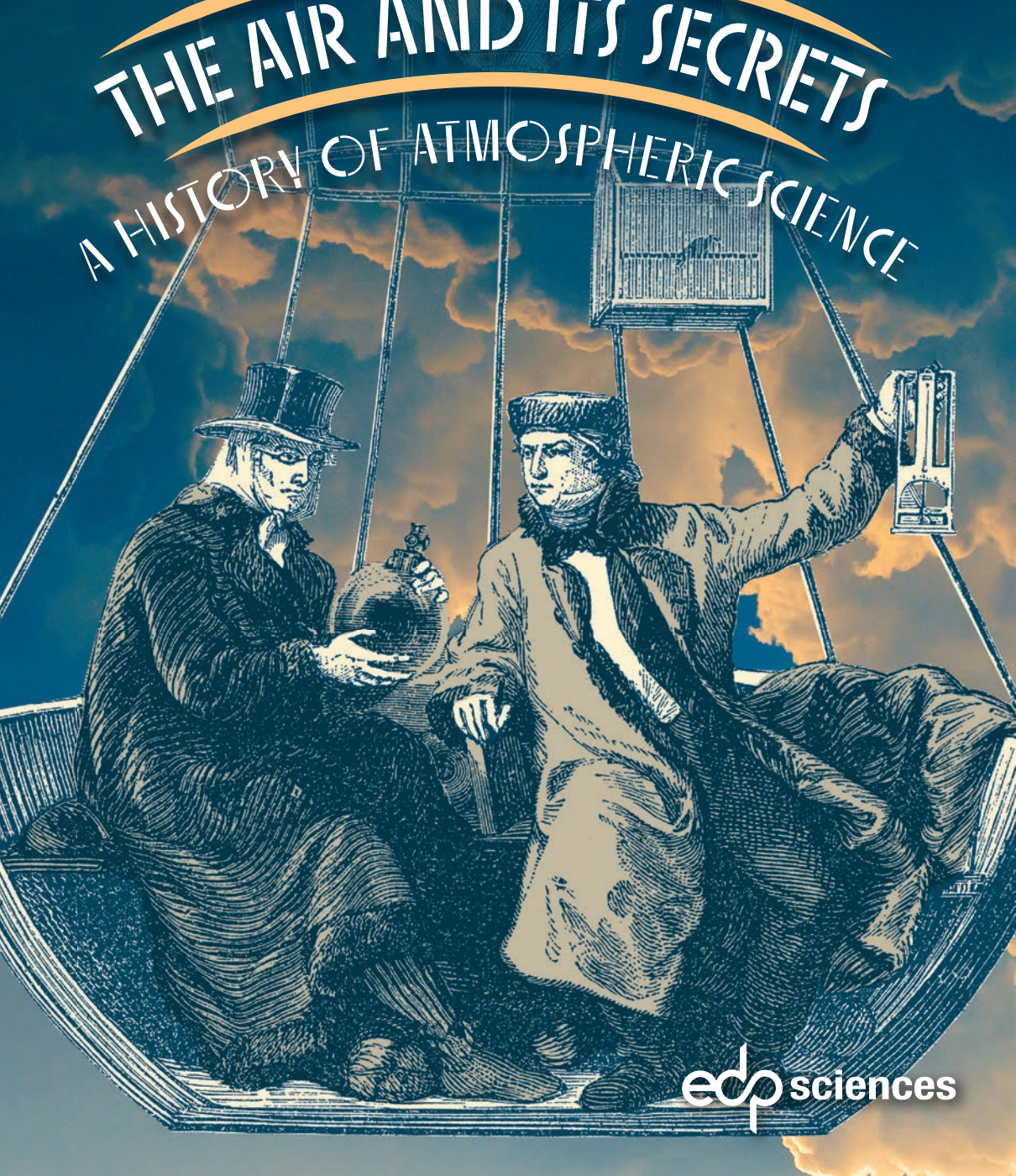


SCIENCES & HISTORY

Guy P. BRASSEUR

THE AIR AND ITS SECRETS

A HISTORY OF ATMOSPHERIC SCIENCE



edp sciences

THE AIR AND ITS SECRETS

A HISTORY OF ATMOSPHERIC SCIENCE

AIR, this invisible medium that surrounds us, makes life possible. According to Baudelaire, air 'is full of the thrill of things that flee'; indeed, it holds a multitude of secrets that philosophers, naturalists and other scientists have tried to unravel over the centuries. In this book, the author outlines the major scientific advances that have led to the discovery of the physical properties and chemical composition of air, the dynamic properties of the Earth's atmosphere, the mechanisms that lead to the formation of storms and other weather events, and the natural and anthropogenic processes responsible for climate change, ozone depletion and air quality.

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Guy P. Brasseur

The Air and its Secrets

A History of Atmospheric Science

edp sciences

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Cover illustration: In 1804, Joseph Louis Gay-Lussac and Jean-Baptiste Biot measured atmospheric conditions at an altitude of 7,000 metres during a hot air balloon flight.

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Die Natur hat es sich nicht angelegen sein lassen,
uns die Auffindung ihrer Gesetzten bequem zu machen.

Nature did not intend to allow us to easily discover its laws.

Albert Einstein

Letter to Erwin Freundlich, September 1, 1911,
Assistant at the Royal Prussian Observatory in Berlin.

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Foreword

Air is a common good. Closely linked to life, this invisible fluid that surrounds us and forms a layer around the Earth, called the *atmosphere,* belongs to each of us. Therefore, no one should have the right to confiscate it to alter its properties and thus harm the health of living beings. Any lasting disturbance of the physical or chemical properties of the air will alter the equilibrium of the planet, with potentially serious consequences for the future of our societies.

This *invisible ocean* in which we are immersed was wonderfully described in the mid-nineteenth century by the editor of the *Bombay Times* in India, the Scottish journalist George Buist (1805-1860)[1]. For him, the atmosphere is

> "a spherical shell which surrounds our planet to a depth which is unknown to us, by reason of its growing tenuity, as it is released from the pressure of its own superincumbent mass. Its upper surface cannot be nearer to us than fifty, and can scarcely be more remote than five hundred miles. It surrounds us on all sides, yet we see it not; it presses on us with a load of fifteen pounds on every square inch[2] of surface of our bodies, or from seventy to one hundred tons on us in all, yet we do not so much as feel its weight. Softer than the softest down—more impalpable than the finest gossamer—it leaves the cobweb undisturbed, and scarcely stirs the lightest flower that feeds on the dew it supplies; yet it bears the fleets of nations on its wings around the world and crushes the most refractory substances with its weight. When in motion, its force is sufficient to level the most stately forests and stable buildings with the Earth—to raise the waters of the ocean into ridges like mountains, and dash the strongest ships to pieces like toys. It warms and cools by turns the Earth and the living creatures that inhabit it. It draws up vapors from the sea and land, retains them dissolved in itself, or suspended in cisterns of clouds, and throws them down again as rain or dew when they are required.
>
> It bends the rays of the sun from their path, to give us the twilight of evening and of dawn; it disperses and refracts their various tints to beautify the approach and the retreat of the orb of day. [...] It affords the gas which vivifies and warms our frames and receives into itself that which has been

[1] Text quoted by US Navy Lieutenant Maury, M.F., *The Physical Geography of the Sea*, Sampson, Low, Son & Co., 1855.

[2] Approximately 10 tons of air per square meter.

> polluted by use, and is thrown off as noxious. It feeds the flame of life exactly as it does that of the fire—it is in both cases consumed and affords the food of consumption—in both cases it becomes combined with charcoal, which requires it for combustion, and is removed by it when this is over."

The origin of the word *air* must be sought in the Greek and Latin languages, which use the words *ἀήρ* and *aer* (*aeris*) respectively to designate air, mist, fog, wind, breeze, atmosphere, and, more generally, weather. Air is defined as a transparent fluid, odorless and tasteless, weightless, compressible, and elastic. But in its figurative sense, which emerged in the sixteenth century, the word "air" describes an appearance, a look, a resemblance, a way of being, speaking, and behaving, a disposition of mind.

Etymologically speaking, the two terms that best characterize the science of air are *aeronomy* (from the Greek αηρ, air and νομοζ, law) and *aerology* (from the Greek αηρ, air and λογοζ, speech). Both terms have lost their general meaning, however, as aeronomy is specifically concerned with the physical and chemical properties of those parts of the atmosphere in which ionization and dissociation reactions predominate. Aerology, on the other hand, refers to the study of air motions occurring mainly on a synoptic scale in the atmosphere. Today, *meteorology* (μετεωροζ, which is above the Earth and λογοζ, speech) is defined as the science that studies phenomena affecting the lowest part of the atmosphere. A distinction is sometimes made between dynamic meteorology (multi-scale air movements affecting winds and temperature) and physical meteorology (thermodynamic, optical, electrical, and acoustic phenomena, radiative transfer, aerosol, and cloud physics, precipitation). Weather forecasting, covering the next few hours or days, is an important application of this science. Meteorology should therefore not be confused with the study of climate, which deals with the long-term evolution (decades, centuries) of the physical state of the Earth's system. Finally, atmospheric chemistry refers to the chemical and photochemical transformations of compounds in the air, while biogeochemistry describes the cycles of the main chemical elements in the Earth system.

The development of the atmospheric sciences is inseparable from the evolution of scientific thought in general. *Robert*'s dictionary defines science as "any body of knowledge having a definite and recognized object and its own method". As for *Littré*'s dictionary, it offers a shorter definition: "A system of knowledge about a subject." And for science historian Yves Gingras[3],

> "The term science is used generically to designate practices that aim to describe and explain natural phenomena through observation, calculation or measurement."

Scientific research is, therefore, a logical and objective process designed to establish the truth. However, to paraphrase German climatologist Mojib Latif[4],

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[3] Gingras, Y., *Histoire des sciences, Que Sais-je?* Presses Universitaires de France, 128 pp., 2024.

[4] Latif, M. (ed.), *Wert der Wahrheit* (*Value of the Truth*), Herder, Freiburg, 2024. See specifically the article of M. Latif, President of the Hamburg Academy of Sciences, under the title: *Klimawandel: Fakt oder Fiktion*? (Climate change, Fact or fiction?).

Science cannot aspire to absolute truth. Rather, it seeks to provide the best possible explanations of natural phenomena based on knowledge that is nonetheless falsifiable. The absolute truth, as the ultimate state of knowledge is never achieved, because science is a dynamic process. It is based on hypotheses that must be constantly tested, questioned, corrected, or even rejected on the basis of observation and experimentation.

To be fruitful, research must combine the imagination of the researcher with a rigorous approach. It must be independent of external pressures or directives from those in power. However, isn't science, as some sociologists claim, a set of conventions produced by a particular culture, rather than a body of verifiable knowledge and hypotheses? Isn't this science, which claims to be "pure and independent", also a discourse conceived and claimed by the researchers themselves to legitimize their prestige and ultimately reinforce the primacy of Western civilization? Does it not ignore the fact that there are other ways of acquiring knowledge? And, as the French philosopher Bernard Latour (1947-2022), one of the proponents of social constructivism[5] has suggested, isn't our image of reality essentially a product of the human mind rather than a faithful reflection of that reality? Is this image not, to a certain extent, negotiated within economic networks and political institutions? As Dominique Pestre, a specialist in the social and cultural history of science[6] states:

> "The sciences are [...] not driven solely by their autonomous logic of action. They are also defined and shaped by the world around them - they are actors in the social, economic and political world, and they are shaped by them."

At the same time,

> "Science is *the* knowledge system of modern societies, a form of legitimacy for public action, an offer of arbitration proposed to the public arena, and this is why it is often contested."

In the introduction to his book on the political history of discovery[7], Physicist Jacques Blamont (1926-2020) writes:

> "Science is not born of astonishment and the desire to know; it is also born of the will of the powerful. The light of reason has its dark, violent side. [...] The machines we use to make and unmake our world derive from the thirst for conquest, the desire for power over men and things, pride and folly. There is no progress in knowledge that is not linked to the will of a Prince. No scientific revolution that is not rooted in an institution entrusted by a sovereign with the development of knowledge."

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[5] Social constructivism considers that social phenomena are created and institutionalized, then transformed into traditions. This school of sociology was introduced by two Austrian-born American sociologists, Peter L. Berger and Thomas Luckmann, in their book *The Social Construction of Reality* (1966).

[6] Pestre D., *À contre science, Politique et savoirs des sociétés contemporaines*, Éditions du Seuil, 251 pp., 2013.

[7] Blamont, J., *Le Chiffre et le Songe. Histoire Politique de la découverte*, Editions Odile Jacob, Paris, 941 pp., 1993.

In any case, the very concept of science has evolved, and it wasn't until the nineteenth century that the major scientific disciplines covering much of knowledge - physics, chemistry, and biology were coherently constituted. The atmospheric sciences and, more generally, the Earth sciences were born in the wake of these fundamental disciplines.

Scottish chemist William Ramsay (1852-1916), for example, rightly wrote in his book *The gases of the atmosphere*[8] published in 1896:

> "To tell the story of the development of men's ideas regarding the nature of atmospheric air is in great part to write a history of chemistry and physics. This history is an attractive and varied one: in its early stages it was expressed in the quaint terms of ancient mythology, while in its later developments it illustrates the advantage of careful experimental inquiry. The human mind is apt to reason from insufficient premises; and we meet with many instances of incorrect conclusions, based upon experiment, it is true, but upon experiment inadequate to support their burden. Further research has often proved the reasoning of the Schoolmen to be futile; not indeed from want of logical method, but because important premises had been overlooked."

Throughout history, the acquisition of knowledge was initially influenced by beliefs based on divine powers. The first steps toward a more rational approach were directly related to the emergence of the first civilizations, such as Egypt along the Nile, Mesopotamia between the Tigris and Euphrates rivers, ancient Greece around the Mediterranean, and the Orient (China, India, and the Arab world). During the Middle Ages, European science developed from the knowledge of ancient Greece and the Arab world. Europeans benefited from Latin translations of the works of the philosophers who had dominated these ancient civilizations. The first universities were founded in the twelfth century, first in Bologna, then in Oxford, Cambridge, and Salamanca, and were devoted primarily to grammar, logic, and rhetoric (*the trivium*), as well as arithmetic, geometry, astronomy, and music (*the quadrivium*). The teaching method was scholasticism, a synthesis of Greek philosophy and Christian theology. Medieval minds had to choose between reason and revelation, which created considerable tension among the philosophers of the time. As early as the thirteenth century, the English Franciscan Roger Bacon (1214-1294) declared that "no discourse can give certainty, everything rests on experience". Western science really took off in the sixteenth and seventeenth centuries.

Why has it taken so many centuries to unravel the secrets of the air? First, because of the difficulty of identifying the presence of various gases in a transparent, elusive substance that at first seemed more like a spirit, a phantom, or a breath than a physical object accessible to our senses. Secondly, because scientific errors or misunderstandings have delayed the discovery of the true nature of air, for the philosophers of antiquity, the air had the same spiritual character as fire, and for the scientists of the seventeenth and eighteenth centuries, the phenomenon of combustion was explained by the theory of phlogiston. Finally,

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[8] Ramsay, W., *The gases in the atmosphere. The history of their discovery*, MacMillan and Co., Ltd., New York, 1896.

because many believed that nature possesses a creative power over matter; therefore, the idea that "nothing is created and nothing is lost" and, consequently, that mass is conserved in a chemical transformation was not accepted.

The chapters in this book take us through very different periods of history. The earliest studies of the sky and meteors date back to ancient civilizations, particularly the Babylonians, Egyptians, and Chinese. The philosophers of the classical Greek period considered air to be one of the four constituent elements of the universe. The first scientific treatises on meteorology published during this period, especially by Aristotle, served as a reference for the thinking of scholars for several centuries. During the Middle Ages, alchemists were interested in the properties of air, but it was during the Renaissance that a rigorous scientific method was developed, and observation became increasingly important in the work of scientists. The fundamental laws of air compressibility were established, and the movements of the atmosphere were described by mariners sailing around the world. The idea that air was composed of different gases began to take hold. The seventeenth century saw real technological advances with the development of the first meteorological instruments, notably the mercury barometer. In the eighteenth century, alchemy gave way to experimental chemistry with the discovery of the vital gas oxygen and the identification of several other chemical compounds in the air, including nitrogen and carbon dioxide. The nineteenth century was influenced by a resolutely positivist movement that favored the development of modern science, especially scientific meteorology. It was the work of a handful of scientists, mostly working individually. As for the modern period of the twentieth century, although severely shaken by two world wars, it was marked by dazzling technological advances and unprecedented demographic and economic growth. The development of space exploration, information technology, and more recently, artificial intelligence has transformed the scientific landscape. It has enabled researchers, now working in often multidisciplinary teams, to make major advances in Earth observation, weather forecasting, and climate modeling. By the end of the century, there was a growing awareness of the limits to unbridled economic growth and the need to preserve natural resources.

By exploring the scientific concepts used to analyze and predict atmospheric behavior, we will show that discoveries have often been the work of a few extraordinary individuals determined to unravel the mysteries of the natural world. Science is more than an abstract process; it is a source of progress for societies and contributes to the development of civilizations. We highlight the role of researchers, their efforts, ingenuity, critical thinking, patience, and perseverance, as well as the difficulties and struggles they face. This book will allow us to meet some highly talented individuals, learn about their motivations, and understand the importance of their work. By taking a long-term view, we will also emphasize the progressive and cumulative nature of scientific work.

We will try to appreciate the extent to which social, political, and economic factors have influenced research and, conversely, the extent to which scientific progress has influenced society, the ethics of individuals, and, more generally, their conception of the world. We will look at the extent to which scientific

progress has met the norms defined by Robert King Merton[9] (1910-2003) and named the *ethos* of science. For this American sociologist, scientists must promote common ownership of scientific information, foster effective collaborations, and subject the results of research to critical scrutiny. They must also, in a universalist spirit, ensure that the quest for knowledge is not influenced by socio-political situations or the quest for personal gain.

The history of atmospheric sciences illustrates mankind's desire to unravel the mysteries of nature, especially those of the Earth's atmosphere. Today, studies of the atmosphere and the Earth system in general remain exciting areas of research, from the dynamics of the fluids surrounding the planet to air and water pollution, ecosystem health, and climate change. It is through the contribution of science that we will be able to address global challenges and ensure the well-being of the Earth's inhabitants.

This book is not a treatise on history that would follow the traditional standards of a rigorous discipline. It simply highlights some of the discoveries that have led to a better understanding of the properties of the Earth's atmosphere. Rather than presenting an exhaustive list of historical facts, it evokes some important moments in the development of science and places them in the context of their time. The text is therefore not based on a chronological sequence of scientific works but rather presents the contribution of a few scholars who, with enthusiasm and often with very limited resources, have advanced knowledge. Boxes in the text provide the interested reader with scientific details or additional information.

The book consists of twelve chapters. After a preamble entitled "Air and Life", Chapter 1 shows that air pollution is an ancient phenomenon, even if the situation has deteriorated considerably in the last two centuries. Chapter 2 deals with questions related to the conquest of the vertical, which has allowed us to better define the structure of the atmosphere. Chapter 3 looks at the fascinating advances that have made it possible to identify the various gases present in the atmosphere, and Chapter 4 describes the scientific advances that have made it possible to understand the complexity of air motion. Chapter 5 focuses on the specific problems of the upper atmosphere. Chapters 6, 7, 8, and 9 deal respectively with stratospheric ozone, greenhouse gases, atmospheric photochemical processes, and particulate matter. Chapter 10 describes the processes by which humans have disturbed the atmosphere. Chapter 11 traces the evolution of knowledge about climate change. Finally, an epilogue attempts to place advances in atmospheric science in the broader context of scientific and technological development and the political contingencies that have influenced different periods of history.

The book is written for a curious, but not necessarily specialized, readership. It offers students interested in environmental issues a historical framework that will enable them to better understand the evolution of the discipline in which they are engaged. We will often use narrative technique to show that

[9] Merton, R.K., The Normative Structure of Science, in: Storer, N.W. (ed.), *The Sociology of Science*, The University of Chicago Press, Chicago and London, pp. 267-278, 1973 (1942).

each discovery is an exciting adventure, a story that contextualizes the work of the actors involved and captures our imagination. By adopting this somewhat unusual perspective, we hope to show that research is a dynamic and evolving process and that it cultivates critical thinking. It certainly inspires a sense of wonder and curiosity.

The major environmental problems facing our societies today – climate change, the depletion of natural resources, the rapid destruction of biodiversity, and the existence of global pandemics will only be solved by a moral and lasting contract between science and society. Public trust in research is therefore essential if we are to build a genuine alliance between scientists and the inhabitants of our planet. It is therefore the responsibility of researchers to be fully transparent, to show how research is progressing, and to share their data and results. Research means doubt and the right to make mistakes, as well as the satisfaction of success. But in the end, it is the objective validation of research results by peers that must prevail and form the basis of the consensus that society embraces.

Preamble
Air and Life

Ella Adoo-Kissi-Debrah was a young child living with her Ghanaian-born mother, Rosamund, in the Lewisham district of south London. The family's home was located on the South Circular, a busy road in the British capital that exposed the young girl and her mother to high levels of particulate matter in the air. In October 2010, during a trip to the monument commemorating the Great Fire of London in 1660, Ella suffered a severe asthma attack that forced her to cut short her visit. She was treated by the medical profession, but unfortunately, her attacks became more frequent, and her health deteriorated rapidly and inexorably. Despite three years of treatment, Ella, then 9 years old, succumbed to a violent seizure on the night of Valentine's Day, February 15, 2013. Her devastated mother became convinced that it was air pollution that killed her daughter.

The case went to trial in London. The court-appointed experts found that the girl's hospital stays coincided with periods of peak pollution. The public authorities were clearly to blame. It is true that the then Mayor of London, Boris Johnson, had delayed the introduction of low-emission zones for several years. The court concluded that air pollution had contributed to little Ella's death. This was the first time that such a verdict has held a public authority responsible for the death of a person because the authorities, who should have been working to improve air quality, had failed to take adequate measures to protect the health of residents. There had been negligence on the part of the authorities.

It is not only in the United Kingdom that courts are confronted with air quality issues. In France, for example, the *Conseil d'État*, seized by an environmental association in 2017, ordered the government to implement plans to limit air pollution in various areas of the country and to comply with the requirements of European directives on the subject. In the absence of a response from the executive, the administrative court ordered the French state in 2021 to pay a penalty of 10 million euros to various agencies and associations in charge of air quality. The recognition by the courts of the right of every individual to benefit from a quality environment, and therefore to breathe clean air, is an important development in the law of our societies.

These two lawsuits must be seen in a broader context. According to the World Health Organization (WHO), more than seven million people on our planet die prematurely every year because of air pollution. Nearly half of these deaths are

caused by indoor combustion emissions from wood, coal, and kerosene stoves and fireplaces, mostly in third-world countries. Outdoor air pollution is mainly caused by road and air traffic, industrial facilities, energy production, waste treatment, agriculture, and residential activities. According to the WHO, nine out of ten people in the world breathe air containing pollutants that exceed officially accepted standards. Today, air pollution is the environmental issue that most directly affects the health of the world's population knowing that each person breathes about 10 to 15 kg of air per day. It can affect all vital organs. Young children and the elderly are particularly vulnerable. Their exposure to particulate matter (PM) and, to a lesser extent, ozone (O_3), sulfur oxides (SO_2), and nitrogen oxides (NO_2) promotes the onset of cardiovascular and pulmonary diseases (asthma, stroke, heart attack). Ozone promotes chronic inflammation and neurodegeneration. Some pollutants appear to have adverse effects on the nervous system. They can worsen mental health, causing symptoms of anxiety and even depression. Polluted air can contribute to the development of Parkinson's and Alzheimer's disease in adults. Exposure of pregnant women to air pollution can result in premature birth, low birth weight, and impaired brain development with lifelong consequences. Some of these conditions can lead to premature death. This situation, which affects most of the planet's inhabitants, should make us reflect on the idea expressed by the Scottish physician Sir John Pringle (1707-1782), pioneer of modern military medicine and president of the Royal Society[10]:

"*Plus occidit aer quam gladius*" (impure air is more deadly than the sword).

The idea that air pollution could affect human health (and the health of all living things) was first rigorously argued in 1970 by Lester Barnard Lave (1939-2011) in his book *Air Pollution in China: Health Effects, Environmental Impact, and Policy Perspectives*. Lave[11] a professor at Carnegie Mellon University in the United States and a specialist in environmental economics, also quantified the relationship between air pollution and mortality in one hundred American cities. He calculated the economic costs of not taking action to clean the air. He showed that a 50% reduction in air pollution in major U.S. cities would save 1970 $1,222 million in respiratory disease costs and $468 million in cardiovascular disease costs. The article, co-authored by Lave and his student Eugene P. Seskin (1948-2015), was published in the journal *Science*. The article attracted so much political attention that the authors found themselves on President Richard Nixon's "enemies" list. Under pressure, Lave retained his position as an economist only through the personal intervention of Carnegie Mellon's president, who refused to fire him. His work, initially ignored, aroused the interest of public health researchers and led to ambitious research programs in the following decades.

Lester Lave also tackled another issue that generated further controversy and some hostile reactions. In 1995, he argued that while electric cars would improve

[10] The Royal Society is Britain's equivalent of the science academies in other countries.
[11] See Lave, L.B., Seskin, E.P., Air pollution and human health, *Science, 169(3947)*, 723-733, 1970. See also the book by the same authors with the same title, published in 1977 by The John Hopkins University Press.

air quality, they would also create other types of pollution, such as those associated with increased electricity production or disposal of waste from batteries. The debate is ongoing.

A Long-Lasting Pandemic

Let's imagine for a moment that this morning radio and television announced the arrival of a toxic cloud over our country that would cause the deaths of nearly a thousand people over the next week. The media would react immediately, urging people to stay indoors with their windows tightly shut until the toxic cloud dissipated and moved away from the country. Residents who remember the Chernobyl nuclear accident and the arrival of a radioactive cloud over their region would undoubtedly be very concerned. What would happen? Who would be affected? Economic activity would likely grind to a halt, streets would quickly empty, and businesses would be forced to close. Public transportation would cease to function.

This doomsday scenario is imaginary, but can it be called science fiction?

The blanket of polluted air that covers our countries is not an isolated, episodic cloud of pollution that disrupts our lives for a few days, as the fictional media report suggests. In reality, the situation is much more serious: every week, with the utmost indifference on the part of the media, the authorities, and the general public, such a cloud of pollutants hangs over our countries, causing health problems: in France, for example, almost 47,000 premature deaths are attributed to air pollution every year, a figure not dissimilar to the number of deaths caused by the coronavirus in that country in 2020.

Of course, the problem is not confined to England and France. It is now estimated that air pollution causes half a million premature deaths each year in Europe (including about 78,000 in Germany, 84,000 in Italy, 41,000 in the United Kingdom, 38,000 in Spain, 12,000 in the Netherlands, and 9,000 in Belgium) and more than 100,000 deaths in the United States. The toll is even higher in Asia: in China and India, the two most exposed countries in the world, the number of deaths linked to air pollution is nearly 1.2 million each. In Pakistan, Indonesia, and Bangladesh, the number is said to exceed 100,000 per year. In Europe, 83% of deaths are attributed to particulate matter, 14% to nitrogen oxides, and 3% to ozone. Air pollution is now more deadly than alcohol consumption, malaria, or AIDS.

For decades, our society has been facing a true pandemic. A pandemic that originated in the developed world but has now spread throughout the world, affecting people on every continent. The situation is particularly worrying in developing countries, where the poor population is particularly exposed.

The question arises: Why were we so shocked by the death of little Ella in England and yet so indifferent to the deaths of millions of men and women around the world who die prematurely from air pollution? It seems that the mind is more easily moved by a dramatic accident or sudden event than by a continuing or unfolding disaster, however serious. The coronavirus pandemic of the 2020s and 2021s offers a similar example: humanity, initially shocked by

the arrival of an unknown and dangerous virus, agreed to remain indoors for a few weeks. But those same inhabitants soon grew weary of a threat that lasted several months; they gradually ignored the restrictions imposed by governments as the death toll continued to rise. More generally, it seems that our Western societies are incapable of taking seriously the dangers and disasters that slowly or invisibly threaten humanity, such as global warming, the destruction of biodiversity, and air pollution.

In a column published in the New York Times[12] David Wallace-Wells asks: "Air pollution kills 10 million people a year. Why do we accept this situation as normal?" The author of the book entitled *The Uninhabitable Earth* published in 2017, writes with reference to air degradation:

> "It is death, each year, at the scale of the Holocaust. And with fossil fuels continuing to burn, the totals add up: Ten million premature deaths every 12 months is 100 million a decade. It is 400 million in my lifetime.
>
> These figures are staggeringly large—indeed, large enough that they make air pollution appear to be a larger threat to human mortality than climate change, whose most intense impacts lie in the future and which nevertheless generates more intense anxiety than pollution right now. This is a paradoxical-seeming effect, at first. But it is also an illustrative one, since threats often appear larger and more profound the farther off they are, and more manageable and even bleakly routine once they arrive."

In another article entitled *Ten Million a Year* published by the London Review of Books, Wallace-Wells attributes indifference to air pollution to the inequalities that exist in the world:

> "Not all deaths are created equal. In February 2020, the world began to panic about the novel coronavirus, which killed 2714 people that month. This made the news. In the same month, around 800,000 people died from the effects of air pollution. That didn't. Novelty counts for a lot. At the start of the pandemic, it was considered unseemly to make comparisons like these. But comparing the value of human lives is one thing the machine of modern civilization does relentlessly, almost invariably to prioritize and absolve the rich – when, for example, the global supply of Covid vaccines is apportioned primarily to the highest-income countries."

The Evolution of Ideas

Air pollution is only one aspect of a much broader and more fundamental problem. It's about understanding how dynamic, physical, and chemical processes contribute to the state of the atmosphere, what role the atmosphere has played in the evolution of the Earth system, and more specifically, how the gaseous envelope that surrounds our planet has allowed life to evolve and sustain

[12] Wallace-Wells, D., Air Pollution Kills 10 Million People a Year. Why Do We Accept That as Normal? *The New York Times*, July 8, 2022.

itself. Throughout history, the air, which some have described as an elusive, ghostly fluid, has inspired humankind. As far back as antiquity, the Greek philosophers brought us an original vision that we should take note of. Let's pause for a moment to consider the vital role these scholars played in introducing critical thinking and promoting a systematic search for truth.

As early as the sixth century before the Common Era, philosophers of the Ionian school from Miletus, a Greek city on the Aegean Sea along the western coast of Asia Minor (now Turkey), and in particular Thales of Miletus (c. 610-546 BCE[13]), Anaximander (c. 585-525 or 556-480 BCE) and Anaximenes (c. 585-525 or 556-480 BCE) developed ideas that rejected all mythological accounts in favor of a universal vision. For Thales, the water in which the Earth is immersed is the building block of all matter. As for Anaximander, a student of Thales, he believed that it is not water but the *apeiron* (ἄπειρος), defined as "the limitless, the infinite, or the indefinite," that creates and sustains all existence. He also asserts that the Earth floats at the center of the universe in the form of a cylinder around which the stars move in a universal motion. He identifies four elements that can be transformed into each other: fire, Earth, water, and mist. He claims that rain comes from water vapor rising in the atmosphere under the influence of the sun's rays and that thunder, lightning, and hurricanes are due to the winds. To the Greeks of the time, the air was akin to the soul, but according to Anaximander's student Anaximenes, a gifted observer, the air was the primary substance that gives life to all observable phenomena. It can be transformed by condensation, producing the fog and clouds that produce rain. Water solidifies to produce Earth and, in an extreme form, stone. And by becoming rarefied, the air becomes fire. Anaximenes described the Earth as a disk floating on air, covered by a celestial dome in which the sun and moon, also in the form of disks, gravitate.

The Ionian School of Miletus, probably the first philosophical school in history, was founded two hundred years before the golden age of Greek civilization, thus challenging the dominant mystical-religious thinking of the time in favor of the search for new knowledge based on curiosity. Since the sky was the privileged place of the divine, rain and lightning were necessarily produced by Zeus, and wind by Aeolus. Weather forecasting was meaningless since meteorological phenomena reflected the whims of the gods. The naturalistic vision of Thales, Anaximander, and Anaximenes, a veritable blasphemy against Zeus, was a historical breakthrough that paved the way for scientific thought and the rational development of knowledge.

After the revolt of Ionia against the Persians (499-493 BCE), the capture of the main cities of Asia Minor by the latter, the deportation of the population, and the two Median wars that followed (490-479 BCE), the descendants of the Ionic school were no longer to be found in Miletus. One of them was Empedocles (494-434 BCE)[14]. Born in the Greek town of Agrigento in Sicily,

[13] BCE stands for "Before the Common Era". This formulation is more neutral than the expression "Before Christ" (BC) used previously. CE stands for "Common Era" and replaces the symbol AD, which stands for the Latin phrase "Anno Domini".

[14] Legend has it that Empedocles chose a spectacular death by throwing himself into Mount Etna, and that one of his bronze sandals was thrown over the edge of the crater.

this philosopher considered that love and hate give rise to the four "roots of all things": water, Earth, fire, and air. For Empedocles, these four elements represented the material basis of the physical world and explained the phenomena observed on Earth and in the sky. They were represented by Zeus (for fire), Hera (for air), Nestis (for water), and Aidoneus (for Earth). A very similar worldview had already been adopted in Persia around 600 BCE, when the Persian philosopher and spiritual leader Zarathustra, also known as Zoroaster, wrote that the four elements are "essential to all living beings and must therefore be venerated and protected from all contamination". Empedocles emphasized the material nature of air by introducing a notion that would be taken up twenty centuries later by Blaise Pascal (1623-1662).

Leucippus (born in the fifth century BCE) and his student, Democritus (~460-370 BCE) also rejected divine intervention. But their view of the universe differed from that of Empedocles. For these two philosophers, every material body consists of two types of opposing constituents: on the one hand, small indivisible units they call "atoms" (ἄτομος, atomos), and, on the other hand, the absence of atoms, which forms "the void". Atoms move and combine to form the macroscopic objects we observe.

Plato (428-348 BCE) preferred to describe the nature of the universe by combining triangular plane figures that are considered indivisible. These were combined into regular polyhedra to form macroscopic objects. Air, for example, was represented by an octahedron, an eight-sided polyhedron. Fire, water, and Earth were each associated with a tetrahedron (a pyramid with an equilateral triangular base), an icosahedron with twenty triangular faces, and a hexahedron, which is a cube. A fifth element, a "quintessence" called ether, was sometimes added; it occupied the universe of stars. Adopting the vision of Pythagoras (570-500), who challenged atheistic naturalism, Plato nevertheless formulated a cosmogenic thesis tinged with mysticism,

> "In the beginning, the different elements held different places before being ordered in such a way as to form the universe. But then God arranged them by form and number, and made them as much as possible more beautiful and better among what was neither good nor beautiful [...] God used them to build matter."

Yet Plato was one of the most original thinkers in history. He was interested in a wide range of natural phenomena and, following in the footsteps of his master Socrates promoted the search for truth and universal knowledge through dialogue on a variety of philosophical and political topics[15].

[15] Socrates (470/469-390 BCE) is one of the most illustrious thinkers of ancient Greece. Considered to be the founder of philosophy, he was at the origin of a movement that influenced the thinking of both the Christian West and the Muslim East. This promoter of moral philosophy taught in the streets of Athens, conversing with passers-by as he met them. In 399, he was accused of not recognizing the same gods as the state and of corrupting youth. He was sentenced to death. He refused the help of his friends, who offered to defend him, and died after voluntarily drinking the hemlock brought to him by his jailers in the Prison of the Eleven (the prison of the eleven judges in Athenian democracy,

Aristotle (384-322 BCE), a disciple of Plato, added to Empedocles' four elements' qualities (hot and cold, dry and wet) acquired through the forces applied to them. He wrote:

> "There are two kinds of air: one is coarse and full of vapor, like the air we breathe; the other, more subtle, is the ether in which celestial bodies are immersed and in which they accomplish their revolution."

Born in Stagire (now Stavros), a Greek colony on the Macedonian coast, Aristotle was sent to Athens at the age of 17 to join Plato's Academy. Although a Greek citizen, his sympathies for Macedonia, then at war with his country, made him unpopular. After the death of his master Plato, he left Athens and went first to Anatolia, then to the Aegean Island of Lesbos, before joining the kingdom of Macedonia. In 335 BCE, however, he returned to Athens, where he taught for twelve years in the high school he had established near the temple of Apollo Lyceus. One of his students was Alexander the Great. Aristotle is the author of *Meteorologica*, a reference book used well into the Middle Ages. In his treatise, he explains that wind is a movement of air caused by the sun, and that rain is caused by the upward movement of water vapor under the sun. He also claimed that thunder and lightning are natural phenomena and not the work of Zeus. Driven from the city by the death of Alexander (323 BCE), he retired to Chalcis in Evia, to an estate inherited from his mother, where he died at the age of 63.

Plato and Aristotle denied the existence of a vacuum, which they claimed was incompatible with motion. This concept became the norm until the nineteenth century, when English chemist and physicist John Dalton (1766-1844) showed that, as the Hellenistic proponents of atomic theory had claimed, matter was indeed composed of atoms surrounded by a vacuum.

Finally, Theophrastus (371/370-288/287 BCE), a student of Plato born in Eresus on the west coast of Lesbos, contributed to the study of atmospheric phenomena. Head of the Peripatetic School (the philosophical school founded by Aristotle in 335 BCE), at the Lyceum of Athens, he was a gifted teacher whose lectures were attended by hundreds of students. He published two books on meteorology, based in part on observations reported by farmers and sailors of the time. He discovered that the climate was changing.

Plato's Academy, Aristotle's Lyceum, and Theophrastus' School became the first centers of learning where ideas were debated. The synthesis of philosophy and science in ancient Greece created a framework for scientific inquiry that was interdisciplinary in nature, fostering an intellectual environment that shaped the scientific revolution and the subsequent development of modern science. However, even if the Greek philosophers' description of natural phenomena seemed convincing, important problems remained unresolved: how to explain, for example, that, when the Greek engineer Philo of Byzantium (280-220 BCE) had covered a burning candle with an upside-down vessel sealed at its base by water, the flame went out after a few seconds and the water rose in the vessel?

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where Socrates was chained for a month before his death). Socrates' spirit of inquiry and development of the hypothetico-deductive method would later inspire scientists such as Galileo and Newton.

Other cultures, notably India, Tibet, and the ancient city of Babylon used a description of the universe like that of Plato and Aristotle. In their own languages, however, the words "air" and "ether" are sometimes replaced by "wind" and "void". The traditional Chinese philosophy of the five phases (五行, *WuXing*) holds five elements: wood (木 *mù*), fire (火 *huǒ*), Earth (土 *tǔ*), metal (金 *jīn*), and water (水 *shuǐ*). It was concerned with the relationships that exist between different phenomena and emphasized processes of change rather than the phenomena themselves. The description of the world in terms of air, water, Earth, and fire dominated Western thought for almost two thousand years and held back the evolution of knowledge.

Religious dogmatism was another factor that froze knowledge for a long period of obscurantism. During the Middle Ages, the Christian West referred to atmospheric phenomena only through the Bible, and the Catholic Church discredited all new ideas, especially those based on scientific experimentation. It was in the Islamic-Arab world, stretching from the Iberian Peninsula to Persia, that science advanced most rapidly. The Arabs based their work on the achievements of ancient Greece, especially the thought of Aristotle. Europeans would not have access to this knowledge until the Renaissance, a period that gave pride of place to knowledge and freedom of thought.

Air and Life

From the sixteenth century, pneumatic chemists, especially in England, became interested in the respiratory functions of living beings and the phenomenon of combustion. Of course, it had been known since antiquity that air was indispensable for combustion; Anaximenes had declared that

> "Fire is connected with the rarefaction of air, as water is produced by its condensation".

English physicists showed that these processes could not be understood without dividing air into several different elements. According to them, there were many types of air: *Fixed air*, identified in 1756 by Joseph Black (1728-1799) as carbon dioxide (CO_2), *combustible air*, now known as hydrogen (H_2), identified ten years later by Henry Cavendish, *phlogisticated air* (now known as nitrogen N_2) and *dephlogisticated air* (now known as oxygen O_2), discovered by Joseph Priestley (1733-1804) in 1775. The French chemist *Antoine-Laurent de Lavoisier* (1743-1794), interested in the mechanisms of combustion, observed that the calcination of mercury absorbed the "breathable" part of the air, which he later called *vital air* and *oxygen*. He concluded that there was a kind of analogy between the processes of combustion and respiration. Lavoisier, for whom air was an important element of life, added:

> "Breathing is one of the most important functions of the animal economy and, in general, cannot be suspended for any length of time without death being the inevitable consequence."

We now know that air contains a considerable number of different molecules. In addition to the most abundant, such as nitrogen and oxygen, and a few

rare gases, such as argon and helium, air contains compounds that are in trace quantities but can play a very important role. Some of these species are highly reactive and, with the addition of radiant energy from the sun, they generate a variety of processes known as photochemical processes. These affect the composition of the atmosphere and, ultimately, the major equilibria that characterize the Earth system. In addition, chemical species interact with solar and terrestrial radiation passing through the atmosphere, influencing the Earth's energy balance and thus our global climate. The chemical composition of the air is also determined by the exchange of matter between the various components of the Earth system: the atmosphere, the ocean, and the continents, as well as the ecosystems that develop within them. Chemical transformations support the cycles that sustain life on Earth and, more generally, play a role in the long-term evolution of our planet. Aristotle was fond of repeating that

> "there is an invisible principle in the air which is capable of spontaneously creating living beings from decomposing inert matter".

As for the French geographer and anarchist activist Élisée Reclus[16] (1830-1905), he wrote in 1868[17]:

> "Each molecule of gas, sometimes fixed, sometimes free, passes eternally from life to life; in turn, wind, stream, Earth, animal or flower, it is, in spite of its smallness, the symbol of infinite movement. Air is an inexhaustible source from which all living things draw their breath, and an immense reservoir into which all dying things pour their last breath. Under the influence of the atmosphere, all dispersed organisms are born and die. Life and death are equally present in the air we breathe, constantly succeeding each other through the exchange of gaseous molecules. The same elements that escape from the leaves of the tree, the wind carries to the lungs of the newborn child; the last sigh of the dying weaves the brilliant corolla of the flower, composing its penetrating perfumes. The breeze that gently caresses the stalks of the grass will turn into a storm that uproots tree trunks and overturns ships with their crews. Thus, through an infinite chain of partial deaths, the atmosphere nourishes the universal life of the globe."

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[16] Elisée Reclus was a well-known geographer and author of several books, including *La Nouvelle Géographie Universelle*, translated into several languages and distributed worldwide. He was also a militant anarchist who supported the Paris Commune, for which he was sentenced to deportation to New Caledonia in 1871. The sentence was not carried out, however, and Reclus fled to Switzerland in 1872. Twenty years later, while anarchists were under increasing scrutiny, he was offered a chair in geography *at the Université Libre de Bruxelles* (ULB), but his course was suspended in 1893 following the attack on the Palais Bourbon in Paris by the anarchist Auguste Vaillant. This measure against Reclus led to a series of controversies within the ULB and, in 1894, to the creation of *the Université Nouvelle* in Brussels, open to the ideas of "free examination" and where a large number of students followed Reclus' courses. This university closed in 1919 and joined the ULB.

[17] Reclus, E., *La Terre, description des phénomènes de la vie du globe*, Hachette, Paris, 1868.

In fact, contrary to what we observe in the atmospheres of Earth's neighboring planets, Mars and Venus, and as the author of the Gaia hypothesis, James Lovelock (1919-2022), has clearly shown, the chemical composition of Earth's atmosphere is kept out of thermodynamic equilibrium by photosynthesis, which converts atmospheric carbon dioxide (CO_2) into organic molecules and produces oxygen from living matter. Questions about the chemical composition of the atmosphere must therefore be addressed within the broader framework of biogeochemical cycles, with particular attention to the interactions between the atmosphere, the ocean, and the continental biosphere.

However, the development of our contemporary societies has profoundly altered the Earth system, leading the Nobel Prize-winning chemist Paul Crutzen (1933-2021) to speak of a new geological epoch dominated by the impact of human activity: *The Anthropocene*. The production and use of fossil fuels, for example, have generated CO_2 emissions that have permanently altered our climate and environment on a global scale: the concentration of this gas in the atmosphere, which has fluctuated between 180 and 280 parts per million (ppm) over the last 1 million years, has risen from its natural level in less than two centuries to over 400 ppm in 2015. It continues to rise, reaching 430 ppm by 2025. Similarly, the atmospheric concentration of methane, another greenhouse gas whose concentration was about 700 parts per billion by volume (ppbv) in pre-industrial times, reached over 1,900 ppbv in 2023. Other perturbations of the global atmospheric chemical system have also occurred: industrial emissions of sulfur and nitrogen compounds, particularly those associated with fossil-fuel power generation and other industrial processes, have caused acid precipitation that has damaged forests and lakes, particularly in northern Europe, Canada, and now China. In the 1980s, industrial chlorofluorocarbons contributed to the destruction of stratospheric ozone, leading to the formation of an "ozone hole" in Antarctica.

In the following pages, we trace the evolution of our knowledge of the gaseous envelope that surrounds our planet. By invoking brilliant minds, and authors of important works, we will talk about fundamental scientific discoveries concerning the dynamical, physical, and chemical processes specific to the Earth's atmosphere. It is not the ambition of this book to cover the topics exhaustively, but rather to present some elements that illustrate how knowledge has been acquired. This development of knowledge is not "linear". It involves debate, sometimes controversy, and conflict. Progress in science is closely linked to the human relationships that exist among those who devote their lives to the development of knowledge. However, it is the experimental facts that take precedence and put an end, at least for a time, to the uncertainties and disagreements that may exist.

1
Air Pollution: A Long History

Moses Maimonides (1138-1204) was a philosopher, physician, and astronomer whose writings dominated thought in the Middle East during the 12th century and remain authoritative today. Originally from Cordoba in Andalusia (Spain), his Jewish family suffered Islamic persecution at the hands of the Almohad sect from North Africa, and in 1148 he took refuge in Fez, Morocco, before embarking for Palestine (Acre) and eventually reaching the town of Fostat, now in the old city of Cairo, Egypt. Maimonides became the personal physician of Vizier Al-Fadil, the regent of Egypt who replaced Sultan Saladin the Great, who had left to fight the Crusaders from Europe.

Maimonides divided his time between his duties as a physician to the Egyptian court and the writing of his ten books, which testify to the high level of knowledge inherited from the civilizations of the region. The sixth treatise, written by the physician-philosopher, deals with the question of asthma. One of his patients suffered from breathing difficulties and headaches so severe that he was unable to wear a turban. Maimonides, who emphasized preventive medicine, stressed the importance of the climatic conditions in which people lived. The first condition for maintaining health, he said, is fresh air, pure water, and a proper diet. He noted, however, that the air of the city was stagnant, cloudy, and polluted due to the presence of tall buildings, narrow streets, and the discharge of urban waste. Therefore, he added, it is better to choose a residence in an open, airy place and a sunny dwelling on the upper floors of a building. The air should be kept dry and clean and, if necessary, purified with mild perfumes. As Fred Rosner[18] Professor of Medicine at Mount Sinai School of Medicine in New York, points out: for Maimonides, the quality of the air was the first requirement for maintaining the health of the body and mind. The prophetic vision expressed by the physician 800 years before the development of industrial society is of burning relevance in our modern world.

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[18] Rosner, F., Moses Maimonides' treatise on asthma. *Thorax, 36*, 245-251, 1981; and Rosner, F., The life of Moses Maimonides, a prominent Medieval Physician. *Einstein Quarterly Journal of Biology and Medicine*, *19*, 125-128, 2002.

Air Pollution in Ancient Times

Air pollution and its effects on human beings have existed long before the Middle Ages, in which the Maimodines lived. It has been a reality since man first appeared on Earth. Traces of soot on the walls of caves inhabited during the Stone Age, more than ten thousand years ago, and the blackened lungs of mummified bodies during the Paleolithic period testify to intense pollution caused by burning wood for heat and food. In the Neolithic period that followed, dust emissions from mining caused silicosis in miners. But it was with the development of cities, especially in ancient Greece and later in Roman times, that people began to breathe polluted air. Aristotle, for example, complained of unbearable odors in urban areas and demanded that manure be kept more than 2 km away from city walls. These odors led some cities to build sewer systems to remove sewage and human waste.

In Rome, large amounts of particulate matter were released into the atmosphere by residents who used wood for heating and burned land to support agriculture. Air pollution was widespread, and the Romans spoke of *infamis aer* (infamous air). This led the poet Horace (65 BCE- 8 EC) to complain about the blackness of buildings and temples. He wrote:

"Stop for a moment admiring the smoke, wealth and noise of Rome[19]."

The philosopher Seneca (4 BCE-65 EC) reports that Emperor Nero (37-68 EC), in order to preserve his fragile health, had to stay away from the smoke that darkened the sky and the cooking smells that prevailed in Rome. The Roman Senate passed a law prohibiting air pollution: *Aerem corrumpere non licet.* The fire of Rome in 64, which devastated the city for over a week and was rumored to have been ordered by Nero to build a new palace, was an episode of extreme pollution that destroyed two-thirds of the city. In the sixth century, Roman law, on which our societies are largely based, proclaimed access to the air, water, and sea as an inalienable right.

Lead Pollution

Another type of air pollution appeared in ancient times and contaminated all of Europe for over 500 years. Mining, especially in Spain, was the source of metal pollution, especially lead[20]. This metal allowed the Romans to make the pipes needed to move water through their aqueducts, as well as coins and kitchen utensils. Non-corrosive lead was also used in the construction of buildings and ships. Powders containing the metal were used in makeup,

[19] *Omitte mirari beata fumum & opes, strepitumque Romae*, A Mecenas, Ode XXIX, Q. Horatii Placci, Odarum Liber Tertius.

[20] Borsos, E., Makra, L., Béczi, R., Vitányi, B., Szenpéteri, M., Anthropogenic air pollution in the ancient times. *Acta Climatologica et Chorologica*, Universitatis Szegediensis, 36-37, 5-15, 2003.

wine preservation, and even as a contraceptive. Analysis of the chemical composition of ice cores from glaciers in the Alps and Greenland[21,22] shows that atmospheric lead levels at the time were at least ten times higher than natural levels. Mining activity, especially in the Iberian Peninsula, was a major contributor to the emission of lead into the atmosphere and its deposition on the Earth's surface.

For thousands of years, ice cores have imprisoned traces of gases and fine particles that have gradually been deposited on the snow with highly variable intensity over time; ice thus provides us not only with climatic archives but also with indicators of human activity. Traces of lead have also been found in sedimentary layers at the bottom of lakes in northern Europe. They also provide important information about the use of this metal throughout history. Lead mining declined significantly after the fall of the Roman Empire in the fifth century but reappeared during the Middle Ages and the Renaissance. Since the 1930s, lead has been used as a gasoline additive and as an antiknock agent in internal combustion engines; its worldwide use has increased its atmospheric concentration by more than a factor of 100 compared to natural levels. It has been known since ancient times that this substance is highly toxic to humans. Its use as a gasoline additive has been gradually banned since the 1970s.

Ice cores provide another interesting insight into air quality during the Roman period. The work of Swiss scientist Célia Sapart and her colleagues[23] show that the microscopic air bubbles trapped in the ice during this ancient period contained relatively high levels of methane. We now know that the intensity of natural biological sources of this gas (swamps, lakes, estuaries, animal digestion, etc.) increases significantly during warmer periods. However, data analysis shows no significant relationship between methane content and temperature as inferred from the isotopic composition of ice. It is therefore likely that the large-scale domestication of livestock in the Roman Empire, as well as the development of rice fields in China during the Han Dynasty, favored the emission of methane into the atmosphere.

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[21] McConnell, J.R., Wilson, A. I., Stohl, A., Arienzo, M.M., Chellman, N.J., Eckhardt, S., Thompson, E.M., Pollard, A.M., Steffensen, J.P., Lead pollution recorded in Greenland ice indicates European emissions tracked plagues, wars, and imperial expansion during antiquity. *PNAS, 115*(*22*), 5726-5731, 2018.

[22] Preunkert, S., McConnell, J.R., Hoffmann, H., Legrand, M., Wilson, A. I., Eckhardt, S., Stohl, A., Chellman, N.J., Arienzo, M.M., Friedrich, R. Lead and antimony in basal ice from Col du Dome (French Alps) dated with radiocarbon: A record of pollution during antiquity. *Geophysical Research Letters, 46*(*9*), 4953-4962, 2019, https://doi.org/10.1029/2019GL082641.

[23] Sapart, C., Monteil, G., Prokopiou, M., *et al.* Natural and anthropogenic variations in methane sources during the past two millennia. *Nature*, *490*, 85-88 (2012). https://doi.org/10.1038/nature11461.

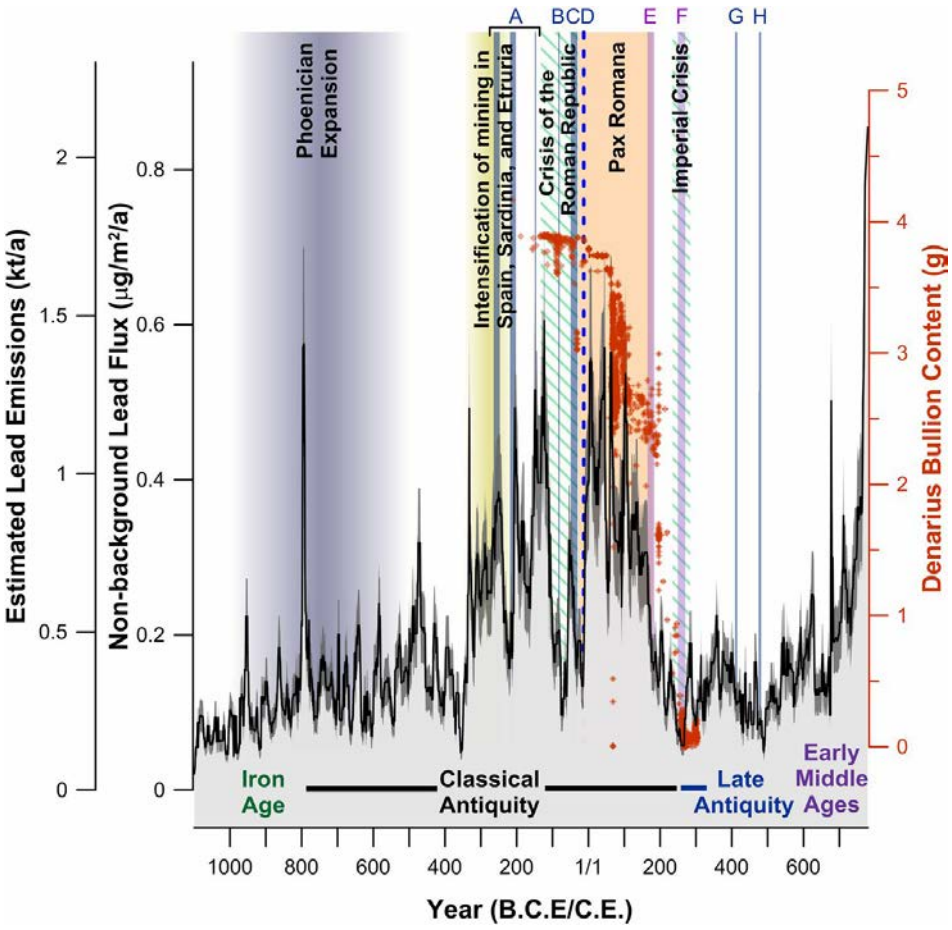


FIGURE 1.1: Lead deposition in Greenland ice and estimates of European lead emissions, silver content of coins, and historical events during antiquity. Also shown are periods of major wars and plagues that would have affected the mining regions of southern Spain, and specific historical events (the Phoenician expansion, the crisis of the Roman Republic, etc.). Reproduced from McConnell *et al.*, Lead pollution recorded in Greenland ice indicates European emissions tracked plagues, wars, and imperial expansion during antiquity, PNAS, 115 (22) 5726-5731, 2018.

The Medieval Period

During the Middle Ages, air pollution, which had eased after the fall of the Roman Empire, became high and worrisome again. First, gaseous emissions and particulate matter produced inside houses, which often lacked efficient chimneys, posed a health problem for the inhabitants. The degraded state of the bone material surrounding the sinuses of the inhabitants' skulls, found in archaeological sites, bears witness to this. Second, the development of

trade, manufacturing, and small industry increased air pollution, especially in cities where labor was available. Discharges outside buildings came from foundries and metalworking, the production of building materials, and the use of ovens to make bricks or bake bread. Open sewers were another source of pollutants.

This was especially true in London, where coal was a major fuel source from the ninth century onward, replacing wood, which had become scarce and expensive due to the gradual destruction of the surrounding forests. It was a low-grade, high-sulfur bituminous coal used for both domestic and industrial purposes. It came from the northeast of England and was transported from the port of Newcastle to London on special ships, earning it the name *seaborne coal*. When burned, it releases not only carbon dioxide (CO_2), but also toxic emissions of sulfur dioxide (SO_2), nitrogen oxide (NO), soot particles, and organic matter. The air in English cities became so unbreathable that in 1257, the mother of King Edward I (1239-1307), Eleanor of Provence (1223-1291)[24] was forced to flee Nottingham Castle to escape the unbearable pollution and seek refuge at Tutbury Castle in central England, where the air was more breathable. A century before, in 1157, Eleanor of Aquitaine (1122-1204)[25] wife of King Henry II had made the same decision for a similar reason. Edward I, therefore, asked local authorities to "take measures to ensure the safety of prelates, nobles and citizens". In 1306, this "ecologist king" banned the use of this low-quality coal, probably one of the first legislative acts in history to suppress the use of a substance in order to protect the health of citizens. It called for the use of alternative materials, especially wood. The new law, which was difficult to enforce, was ignored by residents, who had little choice but to continue to heat and feed themselves. This led his successor, King Edward II (1284-1327), to take draconian measures: those who ignored the decisions were subject to heavy fines, and their stoves and ovens were immediately confiscated and destroyed. In addition, those who didn't comply would be tortured or even sentenced to death. Nevertheless, the population, for whom access to coal was a matter of survival, ignored the warnings, and the city remained heavily polluted for several centuries. It wasn't until the reign of King Henry V (1386-1422) that a commission was set up to control coal imports into London. In 1590, Queen Elizabeth I[26] who said

[24] Eléonore de Provence, of French origin (Aix-en-Provence), wife of Henry III and Queen Consort of England until the King's death in 1272. She was very unpopular among Londoners because she gave positions of influence to members of her family known as Savoyards.

[25] Eleanor of Aquitaine (1122-1204): Queen consort of France and wife of Louis VII until the dissolution of the marriage by the Catholic Church in 1152. They had two children. She then married the Duke of Normandy, who became King Henry II of England, with whom she had eight children. She was imprisoned by her husband from 1173 to 1189 for having encouraged the revolt against the King initiated by her son Henry. She was the mother of Richard the Lionheart, King of England from 1189.

[26] Elizabeth I, Queen of England and Ireland, sometimes called the "Virgin Queen". Daughter of Henry VIII and Anne Boleyn. Anne Boleyn was executed two and a half years after the birth of her daughter Elizabeth.

she was "much disturbed by the taste of smoke," decided to ban the burning of coal in the British capital when Parliament was in session at Westminster.

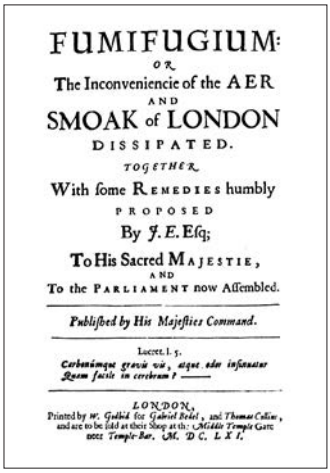
On November 28, 1660, a group of intellectuals, including philosophers, scientists, and physicians, decided to form a learned society, which was recognized by King Charles II (1630-1685) in 1663 as the *Royal Society of London for Improving Natural Knowledge*. The event took place at a troubled time in English history. The king who had succeeded his father, Charles I, executed in 1649, was forced into exile on the European continent after the general dictator Oliver Cromwell (1599-1658) seized power. He had just returned to Britain and restored the monarchy. Among those who helped found the Royal Society was John Evelyn (1620-1706), a cultivated mind who had traveled extensively in Europe and was active in royalist movements. He wrote extensively on a wide range of subjects, including horticulture and vegetarianism. He was particularly interested in gardens, recommending the planting of trees in cities and the development of woods near them. In 1661, while Commissioner for the Improvement of London's Streets and Buildings, he published an exhaustive and well-documented work on air pollution entitled *Fumifugium: or the Inconveniencie of the Aer and Smoak of London Dissipated*[27]. His pamphlet for King Charles II not only explained the problem in precise terms but also offered imaginative solutions and, more generally, a series of measures designed to improve living conditions in the British capital. After discovering that the acidic air hovering over the city had a corrosive effect on the marble and limestone of its buildings, he suggested that the most polluting industries be moved out of the city and that wood be burned instead of coal.

He wrote in his book:

> "Without the use of calculations, it is evident to everybody who looks on the yearly Bill of Mortality that near half of the children that are born and bred in London die under two years of age. Some have attributed this amazing destruction to luxury and the abuse of Spirituous Liquors. These, no doubt, are powerful assistants; but the constant and unremitting Poison is communicated by the foul Air, which, as the Town still grows larger, has made regular and steady advances in its fatal influence."

Despite these cries of alarm, London remained a dirty and polluted city throughout the seventeenth and eighteenth centuries, and it wasn't until the Victorian era (1837-1901) that a sewer system was built: Residents had taken to throwing their garbage into the gutters along the streets at night, and butchers did the same with rotten meat, prompting the great Romantic poet Percy Shelly (1792-1822) to say that the city must look like hell, a smoky, overcrowded city.

[27] Fumifugium: or the disadvantages of London air and fumes.



FUMIFUGIUM:
OR
The Inconveniencie of the AER
AND
SMOAK of LONDON
DISSIPATED.
TOGETHER
With some REMEDIES humbly
PROPOSED
By J. E. Esq;
To His Sacred MAJESTIE,
AND
To the PARLIAMENT now Assembled.

Published by His Majesties Command.

Lucret. l. 5.
Corbemque gravis vis, atque odo infestat
Quam facile in cerebrum? ——

LONDON,
Printed by W. Godbid for Gabriel Bedel, and Thomas Collins,
and are to be sold at their Shop at the *Middle Temple* Gate
next *Temple-Bar*. MDCLXI.

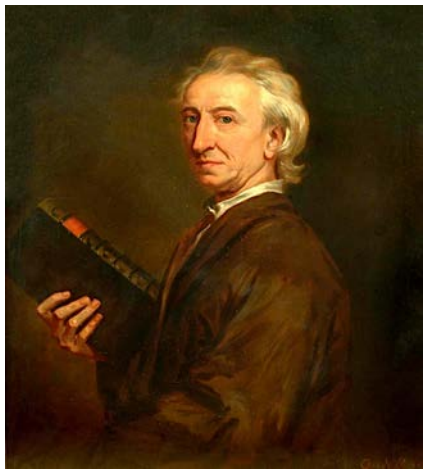


FIGURE 1.2: The cover of John Evelyn's 1661 book on the problem of air pollution in London. Portrait of John Evelyn by Sir Godfrey Kneller (1687).

The Industrial Revolution

Air quality deteriorated even further in the nineteenth century, this time in the wake of the Industrial Revolution. This was made possible by the availability of energy sources and the intensive use of coal. No one thought to protest the use of a mineral that brought wealth and prosperity to those who believed in technological development. Once again, thanks to the large quantities of coal available in England, the country would be at the forefront of industrial progress and would dominate the economic world for several decades. Landscapes changed across the country. Peaceful pastures on the outskirts of cities gave way to industrial plants, and smokestacks belching black smoke appeared in many parts of the country. Railroads were built everywhere, with steam trains carrying vast quantities of coal to the industrial areas. Other countries near Britain also had access to coal. Northern France, Belgium, and Germany became economic powerhouses. The Industrial Revolution also affected the East Coast of the United States, particularly the state of Pennsylvania. So, it is not surprising that air pollution episodes occurred around industrial plants when weather conditions were favorable for air stagnation. In 1873, for example, a thick fog of soot particles from coal combustion descended on London, killing 268 people. As early as 1852, Charles Dickens (1812-1870) wrote in his book *Bleak House*:

> "Smoke lowering down from chimney-pots, making a soft black drizzle, with flakes of soot in it as big as full-grown snowflakes."

As for the French aristocrat Count Alexis de Tocqueville (1805-1859), who visited the industrial city of Manchester in 1835, he painted a very realistic

picture of the living conditions of workers at the time and the air pollution that accompanied industrial development[28]:

> "The employers are helped by science, industry, the love of gain and English capital. Among the workers are men coming from a country [Ireland] where the needs of men are reduced almost to those of savages, and who can work for a very low wage, and so keep down the level of wages for the English workmen who wish to compete, to almost the same level.
>
> Thirty or forty factories rise on the tops of the hills (...). Their six stories tower up; their huge enclosures give notice from afar of the centralization of industry. The wretched dwellings of the poor are scattered haphazardly around them. (...) The land is given over the industry's use. Heaps of dung, rubble from buildings, putrid, stagnant pools are found here and there among the houses and over the bumpy, pitted surfaces of the public places. (...) The fetid, muddy waters, stained with a thousand colors by the factories they pass, of one of the streams wander slowly round this refuge of poverty.
>
> Look up and around this place you will see the huge palaces of industry. You will hear the noise of furnaces, the whistle of steam. These vast structures keep air and light out of the human habitations which they dominate; they envelop them in perpetual fog; here is the slave, there the master; there the wealth of some, here the poverty of most; there the organized effort of thousands produce, to the profit of one man, what society has not yet learnt to give. Here, the weakness of the individual seems more feebly and helpless than even in the middle of a wilderness; here, the effects, there the causes.
>
> A sort of black smoke covers the city. The sun seen through it is a disc without rays. Under this half daylight 300,000 human beings are ceaselessly at work."

The works of the Romantic painter Joseph Mallord William Turner (1775-1851) and the Impressionist painter Claude Monet (1840-1926) also expressively illustrate the intensity of the fog, which became increasingly frequent, dense, and unhealthy during the nineteenth century because of coal pollution. It is likely that the transition from figurative painting to the Impressionist style, characterized by less sharp contours, a lighter palette, and sunsets that tend to be red, was influenced by the changes in the atmospheric environment that accompanied the Industrial Revolution, specifically by the release into the air of large quantities of particles produced by coal combustion.

In the 19th century, the chemical composition of air and water was of particular interest to Scottish chemist Robert Angus Smith (1817-1884), who was also Queen Victoria's first Inspector General responsible for enforcing the Alkali Act. This Act was passed in 1863 to prevent the release into the

[28] Tocqueville's personal notes referring to his visit to Manchester on July 2, 1835. From: de Tocqueville, A., *Journeys to England and Ireland*, Yale University Press, New Haven, CT, 1958.

atmosphere of hydrochloric acid (HCl) produced during the manufacture of sodium carbonate (Na_2CO_3, also known as soda ash). The industrial process had been developed by the French physician Nicolas Leblanc[29] (1742-1806) to support the textile, glass, and paper industries, which used the substance extensively. This technology was used for several years before being replaced in 1872 by a less polluting process developed by Belgian chemist *Ernest Solvay* (1833-1922).

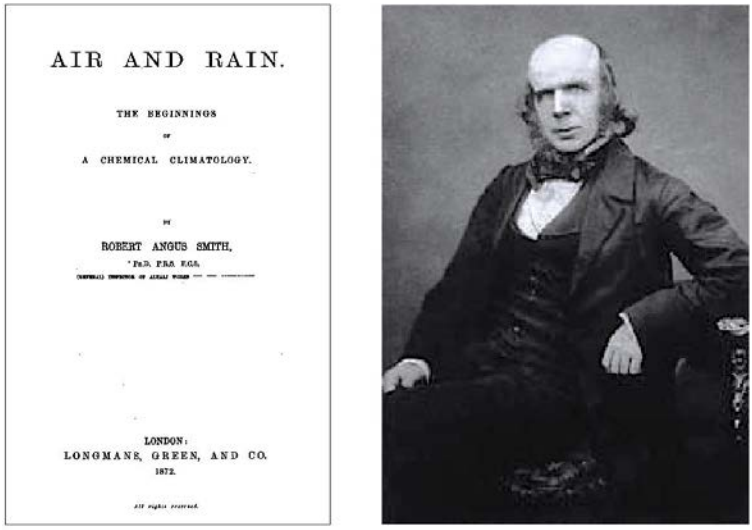


FIGURE 1.3: Robert Angus Smith and his comprehensive book on air chemistry and precipitation, published in 1872.

Smith was a devotee of Spiritualism and had long been attracted to a priesthood in the Church of Scotland. After some hesitation, however, he joined the Manchester Royal Institute, where he became a professor of chemistry. He became a Fellow of the Royal Society and in 1872 published a nearly 600-page study entitled *Air and Rain. The Beginning of a Chemical Climatology*[30] which he dedicated to his German master, the famous Professor Justus von Liebig (1803-1873) of the University of Giessen. It was under the supervision of this great specialist in chemistry applied to biology and agriculture that Smith wrote his doctoral thesis from 1839 to 1841. On his return to England, he became interested in environmental chemistry and demonstrated how complex and

[29] Nicolas Leblanc, French chemist, surgeon and personal physician to Louis Philippe II, Duke of Orléans, won a prize from the Académie des Sciences de Paris in 1791 for his success in producing sodium carbonate from sea salt and sulfuric acid. That same year, he set up a factory in Saint-Denis for the Duc d'Orléans, producing 320 tons of soda a year. The factory was confiscated during the French Revolution, then restored in 1802 by Napoleon. Unable to keep his factory running, Leblanc committed suicide in 1806.

[30] Smith, R.A., *Air and Rain: The Beginnings of a Chemical Climatology*, Longmans, Green and Company, London, 1872.

variable the chemical composition of air can be. In his book, he challenges the oversimplified view of meteorologist and chemist John Dalton (1766-1844), best known for his work on atomic theory[31]:

> "Still, I cannot forget that when I came to Manchester in the last year of Dalton's life, I was reminded of him saying that chemical experiment could not distinguish the air of that city from the air on Helvellyn. Dalton may be called the father of meteorology as well as of strict scientific chemistry, and the saying shows how little that which had been done had affected his mind."

Smith used the analytical methods available at the time to measure the acidity of raindrops. He concluded that the high acidity of precipitation observed in northern England was due to the burning of sulfur-rich coal. In 1872, Angus Smith took up the term *"acid rain"* already used by Hippolyte Ducros (1805-1879), a pharmacist from Nimes, France, in an article published in 1845[32]. Ducros had analyzed the chemical composition of hail collected in front of his house during a violent storm in early 1842 and found that the hailstones contained nitric acid. Smith noted that acid rain attacks the stone and brick of buildings.

In 1904, the treasurer of the Coal Smoke Abatement Society in London, physician Harold (Henry) Antoine des Vœux, wrote a letter to the British newspaper *The Times* in which he suggested that the stale air affecting all Londoners, and especially the intense episodes of urban pollution, should be referred to as *smog.* He believed that London's "pea soup" was made up of toxic fumes rather than fine water droplets. On the other hand, he added, if nothing can be done to get rid of the classic fog episodes that have occurred since the dawn of time, it is quite desirable and even possible to make toxic smoke disappear. He promoted the word *smog*, which he had just proposed, during his lecture on *"Fog and Smog*" at the London Congress of Public Health in 1905[33]. On July 26 of that year, the London *Daily Graphic* quoted Voeux as saying:

> "It required no science to see that there was something produced in great cities, which was not found in the country, and that was smoky fog, or what was known as *'smog'*."

Despite the studies carried out, few concrete measures were taken to limit the deterioration of air quality in the countries that contributed to the Industrial Revolution. Pollution episodes multiplied, especially in winter, and caused many deaths among the population: in Glasgow (Scotland) in 1909, in the Meuse Valley (Belgium) in 1930, in St. Louis (Missouri, USA) in 1939, in

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[31] Dalton's atomic theory states that (1) elements are made up of extremely small particles called atoms; (2) atoms of a given element are identical in size, mass and other properties; atoms of different elements differ in size, mass and other properties; (3) atoms cannot be subdivided, created or destroyed; (4) atoms of different elements combine in simple integer ratios to form chemical compounds; (5) in chemical reactions, atoms are combined, separated or rearranged.

[32] Ducros, M., Observation d'une pluie acide, *J. Pharm. Chim. 3*(7), 273-277, 1845.

[33] However, it seems that the term "smog" was already used in California in the "Santa Cruz and Monterey illustrated Handbook" published in 1880.

Donora (Pennsylvania, USA) in 1948, in London in 1892, then again in the British capital in 1948, 1952, 1956 and 1962. But it was undoubtedly the 1952 episode in London that was the most spectacular and probably the deadliest.



FIGURE 1.4: The creation of factories using coal as a combustion source during the Industrial Revolution caused unprecedented air pollution. Here, the village of Bournville, south of Birmingham in 1926, home to the Cadbury factory established in 1879.
© Wellcome Collection

London's "Great Smog" in 1952

On December 5, 1952, as Londoners awaited the approaching Christmas season, a thick fog descended on the British capital. There was nothing unusual about this time of year, except that the air seemed much more opaque and less breathable than in previous episodes. This smog was characterized by a yellowish color that gave it an acidic character. Residents hunkered down indoors, and sporting events were canceled, except for the legendary off-road race between the Oxford and Cambridge University teams, traditionally held on Wimbledon Common. The opacity of the smog made it dangerous to drive or even cross the street. Some said they could not see the tips of their toes. London's bus service was disrupted, and ambulances transporting the sick, especially victims of severe asthma attacks, stopped operating.

This extremely intense event resulted from the arrival of a powerful high-pressure system over England, accompanied by a temperature inversion[34]. As a

[34] A temperature inversion in the atmosphere occurs when a layer of warmer air is held above a layer of colder air. Such an inversion, common in winter when the ground is frozen, tends to suppress vertical air movements (convection). At low altitudes, it forms a kind of "lid" under which atmospheric pollution remains trapped.

result, the air over the city stagnated for several days. It trapped sulfur emissions and soot particles produced by coal burning in London homes and industrial plants. It is estimated that 1,000 tons of particulate matter and 370 tons of sulfur dioxide were released and trapped in the atmosphere during this episode. The number of people experiencing respiratory distress and asthma attacks increased daily until the smog dissipated on December 9. The cloud of sulfur particles, carried by westerly winds, dissipated over the North Sea. It was later revealed that more than 4,000 people lost their lives in this episode between December 5 and 9, and another 6,000 in the following months. The death rate remained higher than usual until the summer of 1953.

The Prime Minister at the time, Winston Churchill (1874-1965), downplayed the event, claiming that the fog over London would eventually lift. He wanted to give the impression that the economy was working and, no doubt irresponsibly, asked the country to continue burning coal. Apparently, on the morning of December 9, Queen Elizabeth II expressed her disapproval and even considered changing the Prime Minister, which she did not do.

Los Angeles Smog

Smog was not just a problem in London. On July 26, 1943, in the middle of summer, a thick fog suddenly settled over the city of Los Angeles, California. Still reeling from the Japanese Air Force's surprise attack on Pearl Harbor on December 7, 1941, residents were frightened by the phenomenon, which affected their breathing and irritated their eyes, throats, and nostrils. They were convinced it was another act of war by the Japanese, who had spread poison gas over the city. Families hunkered down in their homes or took refuge in local hotels. It soon became clear that the smog was not the result of an external attack but of sources created by American society itself: automobiles and industry. City officials soon believed they had identified the source of the thick cloud. It was the Aliso Street plant of the Southern California Gas Company, which produced an ingredient for synthetic rubber. On July 27, the plant was forced to temporarily shut down. Nevertheless, smog continued to blanket the city. Los Angeles Mayor Fletcher Bowron (1887-1968), however, was reassuring, promising that "the noxious fumes" would disappear from the city's skies within four months. However, smog episodes continued for several decades, sometimes making life unbearable for residents.

Los Angeles has always been considered a sunny city with a Mediterranean climate and clean air, the perfect place to vacation in the shade of palm trees along the Pacific Ocean. The city was also home to a large population of patients seeking treatment for asthma and tuberculosis. But in this extravagant city, crisscrossed by several freeways, the air was becoming increasingly polluted, visibility was getting worse, and the rate of respiratory disease was getting higher. The nature of this pollution, however, was very different from the smog that characterized Europe or the industrial cities of the U.S. East Coast. In Los Angeles, the episodes occurred mainly in the summer, while in London, they occurred mainly in the winter. Furthermore, it was not sulfur particles that were



FIGURE 1.5: Motorcyclists in Los Angeles in the 1950s wearing masks to protect themselves from smog during an air pollution episode.

responsible for these episodes, but ozone, an oxidant that is harmful to human health. This chemical substance was not emitted directly by any human activity; it was produced *in situ* in the atmosphere by photochemical processes that were unknown at the time. In the 1940s, therefore, the question arose: what were the mechanisms behind these episodes of air pollution in California?

The answer came from a Dutch chemist, Arie Haagen-Smit (1900-1977). Originally from Utrecht in the Netherlands, where he wrote his doctoral thesis on sesquiterpenes, certain organic compounds emitted by vegetation, Haagen-Smit joined the prestigious California Institute of Technology (Caltech) in Pasadena in 1937, where he became a professor in 1940 and director of the Environmental Plant Laboratory. There, he became interested in the chemicals responsible for the odors produced by plants and the harmful effects of California smog on the health of agricultural crops. His most important discovery concerned the chemical mechanisms leading to the formation of smog in the Los Angeles area. Haagen-Smit hypothesized that ozone, which was present in large quantities in the city's air, resulted from chemical interactions between partially burned hydrocarbons and nitrogen oxides. These pollutants were found in automobile exhaust and in industrial emissions of combustion products. His hypothesis was immediately challenged by the Stanford Research Institute, a pro-automobile organization founded by the oil industry. This institution attempted to discredit Haagen-Smit's thesis, but subsequent studies confirmed the original conclusions. The atmospheric ozone observed near the Earth's surface was indeed the product of complex chemistry initiated by hydrocarbon and nitrogen oxide

emissions, and its formation was favored by the presence of solar radiation. This explains why ozone is more abundant in summer than in winter. The geography of the area, with mountains to the east and north and the ocean to the west, as well as the recurrence of certain meteorological situations, creates conditions conducive to air stagnation. Primary pollutants released into the atmosphere are then trapped near the ground in the Los Angeles Basin, and under these conditions, secondary pollutants such as ozone and certain particulate matter rapidly form. At the time, the photochemical mechanisms that lead to ozone formation were poorly understood, and it wasn't until the 1970s that significant progress was made. In the 1950s and 1960s, smog episodes occurred nearly 200 days a year. Haagen-Smit, sometimes colloquially known as "Haagen-smog," was chosen by then-California Governor Ronald Reagan (1911-2004) to be the first chairman of the California Air Resources Board in 1968. However, it was not until several years later that California enacted standards to limit pollutant emissions from automobiles; similar regulations were later adopted by the U.S. federal government and many other countries around the world.



FIGURE 1.6: Chemist Arie Haagen-Smit, photographed at Caltech in May 1961. Source: Archives, California Institute of Technology.

Air Pollution in Other Parts of the World

The history of air pollution doesn't end there. The sources of polluting gases have multiplied over the last century with economic development, population growth, diversification of industrial processes, urbanization, development of road, sea, and air transport, intensification of agriculture, etc. Among the so-called *primary* pollutants, i.e. those emitted directly into the air, we should mention sulfur oxides from the combustion of fossil fuels, especially coal; nitrogen oxides, another combustion product, emitted in significant quantities by car, ship, and aircraft engines; and ammonia, which is also present in vehicle exhausts, but mainly comes from the treatment of waste and refuse, the use of nitrogen fertilizers and animal

waste. There are also a large number of carbon compounds, including carbon monoxide, a product of incomplete combustion, and other organic compounds, including alkenes, aromatic hydrocarbons (benzene, toluene, xylene), and formaldehyde. The latter are used in many applications, such as solvents and paints, and are also emitted by car engines. Finally, pollutants include greenhouse gases, especially carbon dioxide, methane, and nitrous oxide, and particulate matter in the form of smoke and elemental carbon. Some particles are also mobilized and released into the atmosphere by air turbulence or mechanical processes.

Urbanization and the emergence of megacities (urban areas with more than 10 million inhabitants) have been the source of numerous pollution episodes in many regions. For many years, Mexico City was considered the most polluted city in the world, with concentrations of air pollutants well above the standards recommended by the World Health Organization. It was a professor at the National Autonomous University of Mexico (UNAM), Humberto Bravo Alvarez (1930-2017), who played a pioneering role in addressing the problem. In the 1950s, following the example of his colleagues in Los Angeles, this specialist, who until then had been interested in the acid rain that was damaging the region's Mayan monuments, carried out the first measurements of the pollutants that characterize photochemical smog in the region. He relied on the work of UNAM meteorologist Ernesto Jáurequi Ostos (1923-2014), a specialist in urban climatology with degrees from the University of California in the United States and the University of Bonn in Germany. Since then, important work has continued with the participation of Mexican scientists, including the Nobel Prize-winning chemist Mario Molina, Louisa Molina, and numerous foreign researchers. Measurement campaigns carried out by international teams have provided new data that have enabled local authorities to take measures to improve the air quality in a metropolis that now hosts more than twenty-two million inhabitants.

Table 1.1. Air pollution standards. World Health Organization recommendations for 2021.

Pollutant	Average period	Pollution standard
PM_{10}	1 day 1 year	45 µg/m^3 15 µg/m^3
$PM_{2.5}$	1 day 1 year	15 µg/m^3 5 µg/m^3
O_3	Maximum 8-hour daily average High season	100 µg/m^3 60 µg/m^3
NO_2	1 hour 1 day 1 year	200 µg/m^3 25 µg/m^3 10 µg/m^3
SO_2	10 minutes 1 day	500 µg/m^3 40 µg/m^3
CO	1 hour Maximum 8-hour daily average 1 day	30 mg/m^3 10 mg/m^3 4 mg/m^3

Note: Annual and high-season exposure is long-term exposure, while 24-hour and 8-hour exposure is short-term exposure.

In China, the problem of urban pollution became acute in the 1990s, especially in the three most urbanized areas: Beijing, Shanghai, and Guangzhou. Chinese scientists have been aware of the problem since the 1960s. The pioneer was Xiaoyan Tang (1932-2025), a professor at Peking University and now a member of the Chinese Academy of Engineering. Madame Tang, who began her career working on fundamental issues in chemistry, was intrigued by a statement made by her country's premier, Zhou Enlai (1898-1976). Zhou wanted Chinese scientists to play a more prominent role in the issues facing their country. "I was deeply moved by this statement," said Madame Tang. "I thought that environmental chemistry could be of great importance to the country by providing the information needed to reduce the impact of air pollution on future generations".

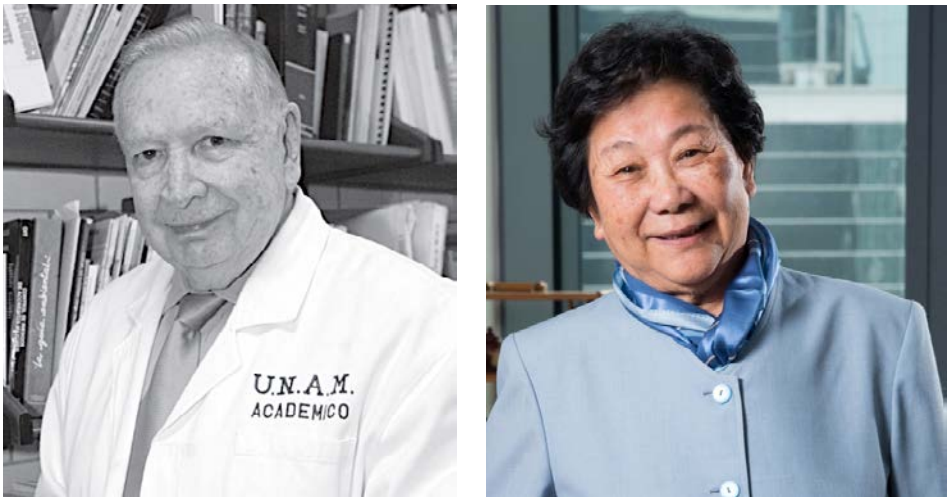


FIGURE 1.7: Two pioneers in air pollution research: Humberto Bravo Alvarez in Mexico and Xiaoyan Tang in China.

In 1974, Renming Wu, a former student at Peking University who had noticed that the air was polluted every summer in the Lanzhou region, an industrial city in a semi-arid zone of northwestern China, invited Madame Tang and her team to visit the area and investigate the causes of the persistent haze that covered the region. The task was daunting, however, as the Chinese teams had only a few rudimentary measuring instruments at the time. Nevertheless, the expedition paved the way for more thorough and comprehensive research on photochemical smog in China. Today, due to the seriousness of the problem and its impact on public health, many universities and research centers are dedicated to air pollution issues, with sophisticated measurement systems and powerful mathematical models. Recent measures taken by the Chinese government, based on scientific studies conducted in the country, have resulted in a significant reduction of particulate matter levels in the country, especially in urban and industrial areas. Atmospheric concentrations of other primary pollutants have also been reduced. However, ozone levels are still too high in the summer.



FIGURE 1.8: The team of Chinese scientists who conducted the first photochemical smog measurement campaign in Lenzhou in 1981. From left to right: Tang Xiaoyan (Peking University), Wang Wenxing (Shandong University), Huang Jianguo (Lanzhou University), Ren Zhenhai (Chinese Academy of Environmental Sciences), Chen Changhe and Peng Xian'an (both Lenzhou University).

Similar studies of the chemical composition of urban air have been conducted in most major metropolitan areas on all continents. Environmental protection laws and policies have been introduced in most countries to significantly reduce pollutant emissions. However, despite very strict standards set by the World Health Organization, there are still regions of the world that are severely affected by air pollution, particularly in Asia and Africa, where millions of people do not have access to clean air. Today, the world's most polluted cities are in India and Pakistan. Rapid population growth in Africa has led to fears that the continent's air quality will deteriorate rapidly. The situation in Europe and North America remains worrying, with pollution levels often exceeding legal limits.

The Tragedy of the Commons and Ecological Equity

Every citizen must be able to live and work in a quality environment. Everyone must be able to preserve their health and enjoy conditions conducive to their personal development. Everyone must have free access to *common goods* such as air, water, ecosystems, and energy sources, which are necessarily limited on our planet and cannot be appropriated exclusively by anyone.

The conflicts that exist between the interests of those who appropriate these resources and the need to preserve the common good were already noted by the Greek philosopher Aristotle, who wrote

> "What is common to all is the object of less care, because men are more interested in what belongs to them than in what they have in common with their fellow men."

The concept of the *tragedy of the commons* was introduced in 1833 by the British writer William Forster Lloyd (1794-1852), a specialist in economic theory and a Fellow of the Royal Society. It referred to a situation in which certain individuals or groups who have access to a public resource act in their own self-interest and end up depleting that resource.

The term "commons" was popularized by microbiologist[35] Garrett James Hardin (1915-2003) in *Science Magazine* in the late 1960s. This text was a major contribution to the development of ecological thinking at the end of the twentieth century. Since then, several options have been proposed to protect the commons: nationalization of natural resources and thus state control over consumption; privatization of these resources to encourage owners to manage them rationally and within limits; and finally, resource management by local communities through social norms and institutional arrangements. In 2009, Americans Elinor Ostrom (1933-2012) and Olivier Williamson (1932-2020) were awarded the Nobel Prize in Economics for their analysis of the economic governance of the commons.

The Industrial Revolution not only produced the chemical air pollution we have already mentioned but it also created great inequalities between the social classes exposed to the sometimes very harmful effects on the environment. In many cases, the urbanization of cities was designed to protect wealthy populations from the harmful effects of pollution, while less affluent residents were often the first victims of industrial discharges. American environmental policy expert Robert D. Bullard, often considered the founding father of the environmental justice movement, has this to say on the subject:

> "Any time our society says that a powerful chemical company has the same right as a low-income family that is living next door, that playing field is not level, is not fair."

The concept of environmental justice originated in the United States following the protests initiated in the early 1960s by labor leader and civil rights activist Cesar Chavez (1927-1993). The goal was to end the use of toxic

[35] Hardin, G., The tragedy of the commons. *Science, 162*(*3859*), 1243-1248, 1968.

chemicals, especially pesticides, which were applied to farmland in large quantities and directly affected the health of farm workers. This was the era of DDT[36] which was synthesized in 1874 by Austrian chemist Othmar Zeidler (1850-1911). Insecticide was discovered in 1939 by Swiss chemist Paul Hermann Müller (1899-1965)[37] to preserve crop from the spread of diseases such as typhoid and malaria.

Rachel Carson's (1907-1964) groundbreaking 1962 book, *Silent Spring*, indicted DDT. According to Carson, this product not only caused the death of many farm animals, it was also responsible for the development of cancer among humans. Despite protests from the chemical industry, which accused Carson of taking people back to the darkness of the past, this book called for a scientific approach to addressing and solving this public health problem. Most importantly, it helped launch the environmental movement in the United States and other countries. Although questions of ecological equity are not directly addressed in Carson's book, it soon became clear that marginalized communities, people of color, indigenous peoples, and low-income residents, mainly in rural areas, were the first to be affected. It took charismatic leaders like Cesar Chavez and Martin Luther King Jr. (1929-1968) to highlight the environmental injustices affecting disadvantaged populations. DDT, whose harmful effects can last for generations, was banned in the United States in 1972. It was banned in most other countries under the Stockholm Convention on Persistent Organic Pollutants, which was signed in 2001 and took effect in 2004. Even today, the limited use of DDT helps control the spread of malaria epidemics in certain tropical countries.

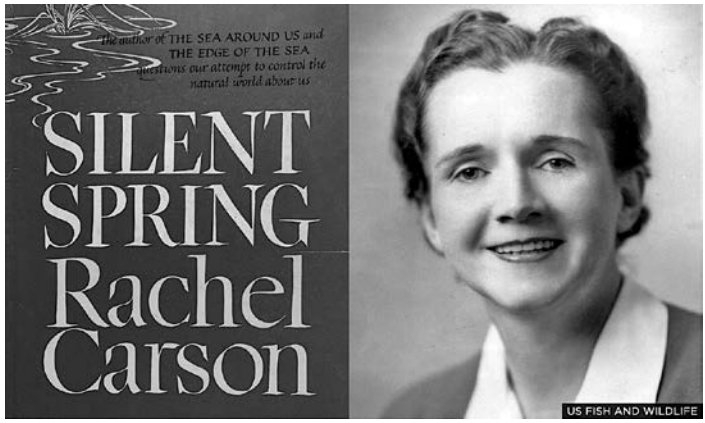


Figure 1.9: Rachel Caron's groundbreaking 1962 book on the evils of DDT, which spurred the development of the environmental movement in the USA. ©Union of Concerned Scientists.

[36] Dichlorodiphenyltrichloroethane.

[37] For this discovery, the Swiss chemist was awarded the Nobel Prize for Medicine in 1948.

The social movement for ecological justice gained strength in the USA in the 1980s. It was heavily influenced by the American civil rights movement and supported by certain churches. It called for an end to "ecological apartheid" and "environmental racism" that disproportionately affected communities of color, who often lived near industrial facilities, highways, and ports. Demonstrations were organized to oppose, among other things, the construction of toxic waste dumps in disadvantaged neighborhoods. In December 1984, the world was horrified to learn of the release of forty tons of methyl isocyanate into the atmosphere in Bhopal, India. More than 6,000 people died near the *Carbide India* plant where the accident occurred, and 500,000 residents were severely contaminated[38].

On February 11, 1994, U.S. President Bill Clinton signed an executive order entitled "Federal Actions to Improve Environmental Justice for Low-Income and Minority Populations". Other countries are beginning to recognize the dangers of air and water pollution, but in many cases, the problem of environmental inequality is being ignored.

Today, the U.S. Environmental Protection Agency, created in 1970 by President Richard M. Nixon (1913-1994) under pressure from the environmental movement, defines *environmental justice* in these terms:

> "The fair treatment and meaningful involvement of all people regardless of race, color, national origin, or income with respect to the development, implementation, and enforcement of environmental laws, regulations, and policies."

Equity means that no group of people, including any racial, ethnic, or socioeconomic group, should bear a disproportionate share of the negative environmental consequences of industrial, municipal, and commercial operations, or the implementation of federal, state, local, and tribal programs and policies.

The issue of ecological inequality also has a geopolitical dimension, since access to natural resources is often limited to a few powerful states, to the detriment of poorer states, to which there is a real ecological debt. This is the case of the countries of the "Global South", whose resources have been abusively exported to the countries of the North.

[38] Synthesized in 1957, methyl isocyanate (CH_3–N=C=O) is a powerful, highly toxic and allergenic insecticide.

2
The Conquest of the Vertical

According to the *Littré* dictionary, "air is an invisible fluid, transparent, odorless and tasteless, weighty, compressible and elastic, which forms a layer around the Earth called the atmosphere". The dictionary adds that "ancient chemistry gave the name air to all the aeriform fluids that we now call gases". An old edition of the *Larousse* dictionary defines air as "an elastic fluid that we breathe," while a more recent edition states that air is "a mixture of several gases (mainly nitrogen and oxygen) that forms the atmosphere". These definitions are very similar to those given in the seventeenth century by the Irish-born philosopher Robert Boyle (1627-1691), one of the founders of modern chemistry. In his book *The General History of the Air*, published in 1692, he stated[39]:

> "By the *Air,* I commonly understand that thin, fluid, diaphanous, compressible and dilatable Body in which we breath, and wherein we move, which envelops the Earth on all sides to a great height above the highest Mountains; but yet is so different from the *Aether* [or *Vacuum]* in the intermundane or interplanetary Spaces, that it refracts the Rays of the Moon and other remoter Luminaries."

Boyle noted, however, that air is not a pure medium

> "The schools teach that air is a warm, moist element; and if it is an element, it must, according to their principles and those of most other naturalists, be a simple, homogeneous body. But, because such elemental or uniform purity is much easier to find in the writings of the scholastics than among the works of nature, many modern philosophers have rightly abandoned to some extent this doctrine of the elemental simplicity of air; but perhaps very few of them, if any, have asserted that air is a compound body, which, in my opinion, it is. Indeed, many of them admit that the atmosphere is not totally pure, but think that it differs from true and simple air, just as water that is a little troubled differs from water that is clear and calm. But for my part, I confess that I don't agree with any of these notions. [...] Speaking of the air in which we men live and breathe, I consider that our atmosphere consists not only of

[39] Boyle, R., *The General History of the Air*, Awnsham and John Churchill, London, 1692.

pure ether, but in large part of a vast multitude of effluents emitted by the terrestrial globe and the various bodies of which it is composed, and perhaps also in part of the substantial emanations of celestial bodies; what makes the atmosphere different from such pure air, as the Schools tell us, is not a naked, indeterminate feculence, but a confused aggregate of several distinct kinds of effluence."

The impurities contained in the air lead to health effects:

"Without the use of calculations, it is evident to everybody who looks on the yearly Bill of Mortality that near half of the children that are born and bred in London die under two years of age. Some have attributed this amazing destruction to luxury and the abuse of Spirituous Liquors. These, no doubt, are powerful assistants; but the constant and unremitting Poison is communicated by the foul Air, which, as the Town still grows larger, has made regular and steady advances in its fatal influence."

As for French chemist Edme Jean Baptiste Bouillon-Lagrange (1764-1844), professor and later director of the *École de pharmacie in Paris*[40], he wrote in 1808 in his *Cours de Chimie*:

"The atmosphere is the mass of air that envelops the Earth's surface: it is composed of several substances. [...] The general properties of air are to be fluid, invisible, insipid, heavy, elastic, incondensable to liquor by cold, to have affinity for a large number of substances, to move with a speed equal to that of the Earth's rotation or with speeds different from this same rotation, and to be easily set in vibration by vibrating bodies."

The definition given in standard dictionaries is probably a bit too restrictive. Air is indeed a compressible fluid that surrounds the Earth, but in addition to gaseous substances (mainly nitrogen and oxygen), it also contains liquid particles (aerosols, cloud droplets, raindrops) and solid particles (dust and ice particles). As a result, air masses are not completely transparent, as particles suspended in the atmosphere sometimes greatly reduce visibility. What's more, stale air can be odoriferous; when walking in the woods, one can smell the scent of gases emitted by vegetation. Air is therefore a complex fluid containing a large number of chemical elements, which we'll try to identify in the following pages. It should be noted that similar envelopes containing various gases and fine particles surround other celestial bodies, but the physical characteristics and chemical composition of planetary atmospheres are very different from those of the Earth. The composition of the Earth's atmosphere is special because it is directly influenced by living matter, which keeps it far from the thermodynamic equilibrium observed on other planets. However, our knowledge of the structure and properties of the fluid that surrounds our planet has progressed slowly over the centuries.

[40] Bouillon-Lagrange owned a pharmacy in Paris, accompanied Napoleon as military pharmacist on his campaigns and became personal physician to Empress Josephine.

Box 2.1. What is a fluid?

A fluid can be defined as a substance whose molecules can move *freely* relative to each other in the case of a liquid, or *independently of* each other in the case of a gas. The molecular structure of liquids is very different from that of gases: in the former, molecules are close to each other, while in the latter, they hardly interact at all, except when they collide. Unlike solids, fluids adapt to the environment in which they are contained. Fluids flow under the effect of the forces applied to them. A distinction is made between external forces, such as gravity, which apply to the entire volume of fluid, and internal surface forces, such as pressure and friction due to fluid viscosity.

Fluids are characterized by different physical quantities: pressure, which represents a force per unit area, density, i.e., the mass of the fluid per unit volume, and temperature. In the case of a so-called perfect gas, these three quantities are linked by a law which states that the pressure of the gas is proportional to the product of its density and its absolute temperature. The motion of a fluid is described by the velocity (direction and intensity) of all its particles. Fluid dynamics consists of determining the deformations of a fluid under the effect of forces applied to it.

The Weight of Air

Aristotle liked to repeat that everything in the universe has weight, except fire, which he considered imponderable. But how could we prove that air was indeed subject to gravity? To answer this question, the ancient Greek philosopher devised an experiment that proved highly disappointing. Aristotle weighed an empty bladder, then repeated the procedure with a bladder that had been inflated with air and therefore had a larger volume. Contrary to his expectations, the two weights were exactly the same. Could it be that air has no weight? The explanation came from another Greek scientist, Archimedes of Syracuse (287-212 A.D.), and his famous principle: "Any body immersed in a fluid (such as air) is subject to an upward thrust (force) equal to the weight of the displaced fluid". Thus, the weight of the air in the inflated bladder could not be detected because it was exactly compensated by the thrust exerted on the bladder by the ambient air. Archimedes' principle, therefore, implied that air has a weight, but it took a long time before this problem was finally solved.

The first evidence that the air has a weight originated in France during the seventeenth-century. It was in the small Perigordian town of Le Bugue that a humble country doctor, Jean Rey (~1583-~1645), who had received his "bonnet de docteur" (doctor's degree) from the University of Montpellier on November 22, 1605, was questioned by the Bergerac apothecary, Sieur Jean Brun, who asked

him why the calcination of "two pounds and *six* ounces of estin[41]" produced "two pounds and *thirteen* ounces of a very white lime"[42]:

> "Sir, Wanting these past days to calcinate tin, I weighed two pounds six ounces of the finest English tin, put it in an iron vase adapted to an open furnace, and at high heat stirring it continuously without adding anything, I converted it in six hours into a very white lime. I weighed it to determine the waste, and found two pounds thirteen ounces. This gave me incredible astonishment, as I couldn't imagine where the extra seven ounces had come from. [...] Your beautiful mind, which takes on impulses beyond the ordinary when it wants to, will find something to occupy you here. I beg you with all my affection to devote yourself to finding the cause of such a rare effect."

Jean Rey, who visited the blacksmiths of his region, replied that it was the incorporation of air into the metal during the combustion process that was responsible for the increase in weight measured by the apothecary of Le Bugue:

> "I respond and gloriously maintain that this extra weight comes from the air, which in the vase has been thickened, weighed down, and made in no way adhesive, by the vehement & long-continued heat of the furnace, which air mingles with the lime and attaches itself to its smallest parts."

Thus, contrary to what was thought, the air that combines with burning bodies has mass and therefore exerts pressure. These findings were published by Jean Rey in 1630[43] in a series of twenty-eight essays explaining why the weight of lead and tin increases during calcination. The document was forwarded by the Bordeaux lawyer Pierre Trichet (~1586-1644) to Father Marin Mersenne (1588-1648), an encyclopedically educated cleric belonging to the *Order of Minimes*. Jean Rey's conclusions about the weight of air were widely discussed at a time when scientists were scattered throughout Europe in salons and intellectual circles and frequented the *Minimes* convent near the Place Royale (now Place des Vosges) in the Marais district of Paris. Mersenne, who maintained relations with the philosophers René Descartes (1596-1650) and Pierre Gassendi (1592-1655), corresponded with Evangelista Torricelli (1608-1647) in Florence and Blaise Pascal (1623-1662) in Paris. He tried to repeat Jean Rey's

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[41] The reaction is: $Sn + O_2 \rightarrow SnO_2$. The mass of tin is 119 g and that of O_2 is 32 g. The theoretical increase in mass when tin is completely converted to lime (tin oxide mass equal to 151 g) is therefore 27%. In his experiment, Jean Brun used two pounds and six ounces (1.077 kg) of tin and obtained two pounds and thirteen ounces (1.275 kg) of lime. The increase in mass (198 g or 18.4%) determined by Jean Brun is slightly less than the theoretical value of 27%. At the time, the mass of atoms was unknown.

[42] Rey J., Lettre du Sieur Brun qui a donné fubiect au prefent difcours Les Essays, Edward Arnold & Co, London, 1951, p. 12. See also: Tyburce, B., Du rôle de l'air dans les combustions. Jean Rey, obscure 17th-century physician, precursor of the famous Lavoisier? *L'actualité Chimique*, *344*, 21-27, 2010. What is known as "white lime" is also called "tin ash"?. At the time, the name lime referred to the product of calcination. It is, in fact, a metal oxide.

[43] That is, several years before the experiments carried out by Torricelli in 1643 and by Blaise Pascal and Florent Périer at Puy de Dôme in 1648.

experiment but made a handling error. He therefore questioned the results of the Perigordian doctor and withdrew his support.

Although he was seduced by the experimental methods that appeared during the Renaissance, Jean Rey remained strongly influenced by the teachings of antiquity and denied, for example, the existence of the vacuum. In his fourth essay, he writes[44]:

> "It is quite certain that, within the limits of nature, the void, which is nothing, cannot find its place. There is no power in nature that could have created the universe out of nothing, and none that could reduce the universe to nothing: this requires the same virtue. But it would be different if we could find emptiness. For if it could be here, it could also be there; and if it is here and there, why not elsewhere? And why not everywhere? Thus, the universe could be reduced to nothing by its own forces; but the glory of being able to destroy it belongs to Him alone who was able to create it."

Jean Rey made other discoveries, including the construction of a thermoscope, the forerunner of the thermometer, which he used to take the temperature of his patients.

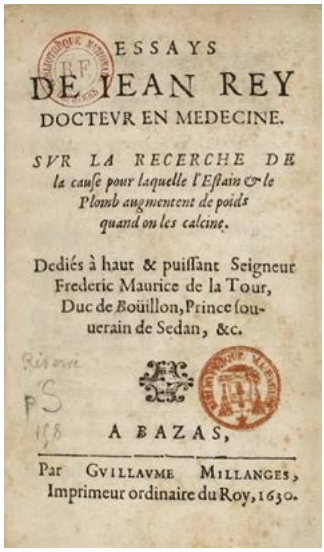

ESSAYS
DE IEAN REY
DOCTEVR EN MEDECINE.
SVR LA RECERCHE DE
la cauſe pour laquelle l'Eſtain & le
Plomb augmentent de poids
quand on les calcine.
Dediés à haut & puiſſant Seigneur
Frederic Maurice de la Tour,
Duc de Boüillon, Prince ſou-
uerain de Sedan, &c.
A BAZAS,
Par GVILLAVME MILLANGES,
Imprimeur ordinaire du Roy, 1630.

FIGURE 2.1: Essays published by Jean Rey in 1630.

Florence's Fountain Builders and Torricelli's Tube

At the same time that Jean Rey published his essays, Florence's fountain builders, who were installing siphons to collect water from the Arno River, found that they were unable to pump the water to a height of more than 32 feet (10 meters), even with the most sophisticated pumps. On July 27, 1630, Italian mathematician Giovanni Battista Baliani[45] (1582-1666), who was interested in aqueduct construction and hydraulic phenomena in general, decided to ask the famous Florentine scientist Galileo Galilei (1564-1642) why pumps were unable to lift water to the top of a 21-meter hill. Baliani, who was also an influential politician in the service of the Republic of Genoa, had been corresponding with his friend Galileo since 1613[46].

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[44] Text written in Old French and slightly adapted.

[45] Captain of the archers in Genoa for almost 25 years, prefect of the fortress of Savona (1611), governor of Sarzana (1623), member of the Senate (1624) and governor of the province of Savona (1647-1649).

[46] In a letter sent to Baliani on March 12, 1613, Galileo explained how to determine the "specific gravity of air", leading A.N. Meldrum, in a letter published on July 30, 1908 in the journal *Nature*, to consider that it was Galileo and not Jean Rey who first introduced the concept of the weight of air.

Galileo played an important role in the development of modern science. He began his medical studies at the University of Pisa but later turned to physics and mathematics. He became a professor at the University of Pisa (1589) and then at Padua (1592). He supported the theory of heliocentrism and contributed to the development of astronomy. He was tried by the tribunals of the Inquisition in Rome for promoting a heretical science. On June 22, 1633, he was forced to admit his errors before the inquisitors at the Convent of Minerva in Rome:

> "I, Galileo Galilei, son of the late Vincenzo Galilei, Florentine, aged seventy, personally brought before this tribunal and kneeling before you, most eminent and reverend cardinals, inquisitors general against heretical depravity throughout the Christian Republic [... ...] have been declared by the Holy Office to be vehemently suspected of heresy, that is, of having maintained and believed that the Sun is the center of the world and immobile, and that the Earth is not the center and moves: desirous of removing from the minds of your Eminences and of all faithful Christians this strong suspicion, reasonably conceived against me, with a sincere heart and unfeigned faith, I abjure, curse and detest the following errors and heresies [....] and I swear that in the future I will never say or affirm, verbally or in writing, anything that could give rise to a similar suspicion against me."

He escaped the death penalty but was sentenced to prison. However, his sentence was commuted, and he was placed under house arrest for the rest of his life in Arcetri, in the hills surrounding Florence. It is said that when Galileo heard the court's verdict, he murmured, "Eppur si muove" (And yet it turns).

It wasn't until 1638, five years after his condemnation by the Inquisition[47] that Galileo gave an answer to the question posed by Baliani; this answer appears in a book entitled *Discourses concerning two new sciences*[48] published in Leiden[49] in the Netherlands. The document is written in the form of a dialogue between three characters: Salviatti, who plays the role of Galileo, and Sagredo and Simplifico, who contradict the master. Salviatti claims that it is the "force of emptiness" (*forza de vacuo*) that prevents the water from rising more than 18 cubits (32 feet or 10 meters). He adds:

> "By weighing the water contained in a tube eighteen cubits long, whatever its diameter, we will obtain the value of the vacuum resistance in a cylinder of solid matter having a bore of that same diameter."

Perhaps influenced by the mechanical engineer Heron of Alexandria, who lived in the first century A.D., Galileo appealed to the notion of the void, a notion rejected by ancient philosophers, especially Aristotle, who believed

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[47] Catholic Church tribunal founded in the XIII^{e} century and operating according to the principles laid down in canon law.

[48] Discorsi e dimostrazioni matematiche intorno a due nuove scienze, 1638.

[49] Since his condemnation by the Inquisition in 1633, Galileo had not been allowed to produce any documents whatsoever. The book was therefore published in a city outside the areas controlled by the Catholic Church.

that nature abhorred emptiness. Referring to Aristotle, Galileo is said to have quipped that "nature abhors a vacuum only up to 32 feet". However, Galileo's explanation is unconvincing and, in fact, incorrect.

After receiving no satisfactory answer, the fountain builders turned to Galileo's disciple, Evangelista Torricelli, whom the Grand Duke of Tuscany, Ferdinando II de Medici, had just appointed official court mathematician. In 1643, Torricelli decided to reproduce a process similar to pumping in his laboratory. To prevent the fluid from being sucked up to a height of ten meters, which was difficult to achieve in the building he occupied, he proposed replacing the water with quicksilver, a liquid metal called mercury, whose density was 13.6 higher than that of water. The engineer Vincenzo Viviani (1622-1703), a collaborator and companion of Galileo, now working for Torricelli, filled a meter-long glass tube with mercury. The tube was hermetically sealed at one end. The scientist then seals the other end of the tube with his finger, turns the tube upside down, and dips the open end into a bowl also filled with mercury. He then removes his finger and observes that the level of mercury in the tube falls and stabilizes at a height of 76 cm. The result of this experiment is fundamental, and its interpretation was probably revolutionary: Torricelli claimed that it was not the force of the vacuum, as Galileo had claimed, but the pressure of the air in the atmosphere that kept the mercury at that height in the glass tube.

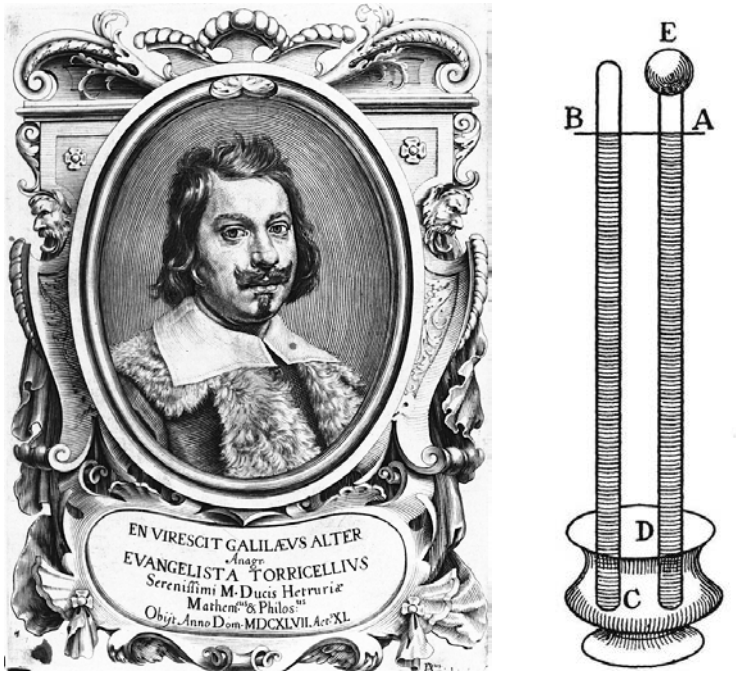


Figure 2.2: Left: Evangelista Torricelli. Source: Wikipedia. https://de.wikipedia.org/wiki/Evangelista_Torricelli. Right: experiment showing that the height of the mercury column is identical in two different tubes. Source: E. Torricelli, *Lezioni Accademiche d'Evangelista Torricelli*. Firenze, 1715, pp. XXVIII.

To demonstrate this property, he repeated his experiment, this time using two glass tubes immersed side by side in the same vat of mercury: one is sealed as before, while the upper end of the other consists of a small glass sphere. If the force of the vacuum were responsible for attracting the mercury upwards, the height of the column of mercury in the two tubes would be different, but this is not the case.

The conclusion was obvious: the pressure exerted by the atmosphere on the surface of the Earth is equal to the pressure exerted by the column of mercury[50]. From this, we can easily deduce that the weight of atmospheric air at ground level is about 10 kg per square meter. And this value is exactly equal to the weight of a 10-meter column of water. The answer to the Florentine fountain builders was therefore clear: water cannot be sucked up from a height of more than 10 meters, no matter what pump is used. This height is determined by atmospheric pressure.

As is often the case in the sciences, some of the discoveries that have profoundly changed knowledge were preceded by work that came very close to them. In fact, the experiment carried out around 1640 by Gasparo Berti (c. 1600-1643), an Italian mathematician and physicist, was very similar to the one carried out by Torricelli a few years later. Berti placed an 11-meter lead pipe along the facade of his house, filled it with water, and sealed both ends. After placing the lower end of the pipe in a tank of water and removing the plug at that end of the pipe, he noticed that the water in the pipe had partially spread into the tank and that the water column had stabilized at a height of 10 meters. Although Berti did not provide a satisfactory explanation for this phenomenon, he had in fact built a large water barometer.

Torricelli's mercury barometer was an essential instrument for meteorology, allowing the science to develop considerably over the following centuries. At the same time (1654), Ferdinand II, also in Florence, invented the thermometer, an essential instrument for meteorologists. A four-volume critical analysis of the qualities and shortcomings of these instruments was published in 1782 by Jean-André de Luc (1727-1817), a citizen of the Republic of Geneva, under the title *Recherches sur les modifications de l'atmosphère*[51]. Torricelli's experiment yielded another equally important result: for the first time, it was possible to create an empty volume that contained therefore no air molecules.

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[50] Commonly used pressure measurement units are the Pascal (Pa), the atmosphere (atm), the bar and the millimeter of mercury (mm Hg). One Torr corresponds to 1 mm of mercury. In common applications, atmospheric pressure is generally expressed in hectopascal (hPa), which corresponds to millibar (mb). Ground pressure is close to 1013.25 hPa or 760 Torr.

[51] de Luc, J.A., Recherches sur les modifications de l'atmosphère contenant l'histoire critique du baromètre et du thermomètre, un traité sur la construction de ces instruments, des expériences relatives à leur usage & principalement à la mesure des hauteurs & à la correction des réfractions moyennes, Chez la Veuve Duchesne, Libraire, rue Saint-Jacques, Paris (tomes 1 à 4), 1782-1784.

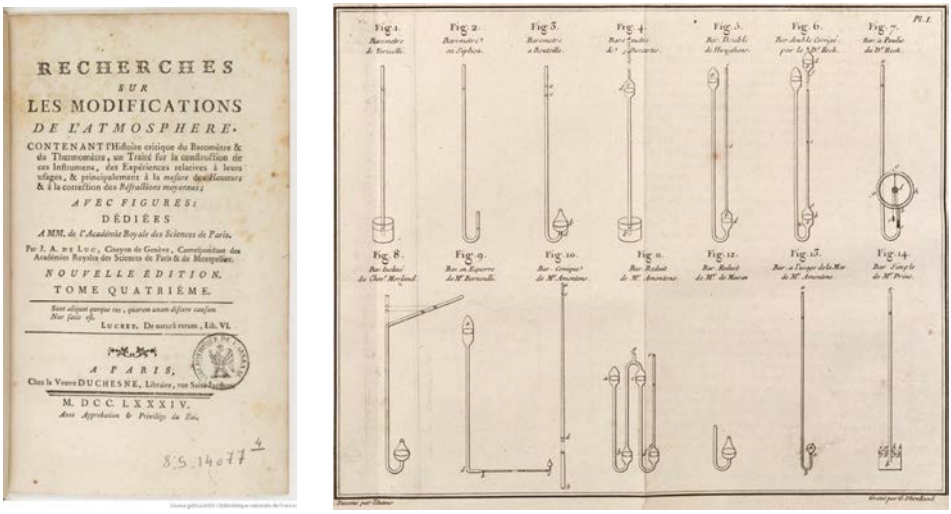

RECHERCHES
SUR
LES MODIFICATIONS
DE L'ATMOSPHERE.
CONTENANT l'Histoire critique du Baromètre & du Thermomètre, un Traité sur la construction de ces Instrumens, des Expériences relatives à leurs usages, & principalement à la mesure des Hauteurs & à la correction des Réfractions moyennes;
AVEC FIGURES;
DÉDIÉES
A MM. de l'Académie Royale des Sciences de Paris.
Par J. A. DE LUC, Citoyen de Genève, Correspondant des Académies Royales des Sciences de Paris & de Montpellier.
NOUVELLE EDITION.
TOME QUATRIÈME.
Sunt aliquæ quoque res, quarum unum discere causam
Non satis est.
LUCRET. De naturâ rerum, Lib. VI.
A PARIS,
Chez la Veuve DUCHESNE, Libraire, rue Saint-Jacques.
M. DCC. LXXXIV.
Avec Approbation & Privilège du Roi.
8°S.14077

Figure 2.3: Book published by J.A. de Luc in 1872-1784 and plate showing different types of barometers built after Torricelli's invention of the instrument in 1643.

In a letter dated June 11, 1644, to his friend Michelangelo Ricci (1619-1682), a mathematician and churchman living in Rome who would become a cardinal at the end of his life, Torricelli wrote

> "I have already drawn your attention to certain philosophical experiments in progress... concerning the vacuum, which are intended not only to make a vacuum, but to make an instrument that will show changes in the atmosphere, which is sometimes heavier and denser, and sometimes lighter and thinner. Many have argued that the vacuum does not exist, others claim that it exists with difficulty, in spite of the opposition of nature; I know of no one who claims that the vacuum exists easily, without any opposition from nature."

And he adds a sentence that will remain famous because it profoundly changes our perception of nature:

> "We live at the bottom of an ocean of the element air, which we know from incontrovertible experiments to have such a great weight that near the surface of the Earth, where it is densest, it weighs about four hundredths of the weight of water[52]."

Rici, who had closely followed Berti's experiments, replied:

> "I estimate that you will unfortunately be too disgusted by the audacious opinion of these theologians and by their constant habit of confusing the things of God with natural questions, where they should instead be treated with greater respect and reverence."

In fact, Torricelli had just put an end to Aristotle's precept, which had been accepted as a "logical impossibility" by all philosophers since antiquity. However, he decided not to publish his results: the rules of natural philosophy were still

[52] The correct value is one eight-hundredth, not one four-hundredth.

under the strict control of the Catholic Church, and only ten years had passed since his master Galileo had been condemned by the Inquisition. It was Father Marsenne, in fact, who would share Torricelli's work with his European colleagues.

It is interesting to note that Baliani had already mentioned the weight of air in a letter to Galileo in October 1630 (more than ten years before Torricelli's discovery):

> "I had come to the idea that there is nothing in the nature of things against emptying. However, it is difficult to do this, especially without violence, but we can find out what the value of this violence must be. We are at the bottom of the immensity of the air, and we do not feel its weight, nor the compression it exerts on us from all sides, because our body has been made by God to resist this compression. This weight, which must be very great, is not infinite: it is therefore fixed. It should be possible to exceed it with a force of suitable proportion, and thus to provoke the vacuum. Whoever wants to find this proportion should know the height of the air and its weight at different heights."

In 1657, an experiment conducted by the mayor of Magdeburg, Otto von Guericke (1602-1686), confirmed the existence of a vacuum. Sixteen horses were



FIGURE 2.4: Above: the statue of Otto von Guericke on a monument in the center of Magdeburg, Germany. The city's mayor is seated next to the two half-spheres used in his experiment. Below: a presentation on the same monument of the experiment confirming the existence of the vacuum. Sources: photos by the author.

unable to separate two air-pumped, hermetically sealed half-spheres. So, von Guericke concluded, it's the external pressure of the air that prevents the two hemispheres from separating, not nature's fear of a vacuum.

Box 2.2. Temperature Measurements

In ancient times, temperature was measured qualitatively using thermoscopes to determine the thermal expansion of a volume of air displacing a column of water. The principle was adopted by the physician *Santorio*, a close friend of Galileo.

In 1654, Ferdinand II de Medici invented a thermometer based on the thermal expansion of wine spirit (ethanol). Around 1700, Isaac Newton (1642-17270) developed the first temperature scale for his linseed oil thermometer: zero corresponds to the temperature of melting snow, and 33 degrees to the temperature of boiling water.

In 1724, German physicist Gabriel Fahrenheit (1686-1736) replaced the thermometer's alcohol with mercury. He established a temperature scale for which 32 degrees corresponded to melting ice and 96 degrees to normal blood temperature. In this scale, the temperature of boiling water is equal to 212 degrees. In 1730, the Frenchman René-Antoine Ferchaut de Réaumur (1683-1757) set the freezing point of water at zero degrees and the boiling temperature at 80 degrees for his alcohol thermometer. In 1742, the Swedish astronomer Anders Celsius (1701-1744) adopted a value of 100 for the freezing point of water and zero for its boiling point for his mercury thermometer. The scale was reversed in 1744.

Blaise Pascal's Experiment

Torricelli concluded his experiments by stating that we live at the bottom of an *ocean of air*[53]. The French theologian and mathematician Blaise Pascal (1623-1662), who took a great interest in the work of his Italian colleague, believed that the weight of air on the planet must necessarily decrease with altitude. He also rejected the idea that nature abhors a vacuum, adding that "he finds it hard to believe that nature, which is neither animated nor sensitive, is susceptible to abhorrence, since passions presuppose a soul capable of feeling them". He therefore proposed to measure the air pressure at different altitudes using a glass tube similar to the one used by Torricelli. On November 15, 1647, he approached his brother-in-law, Florin Périer (1605-1672), a royal counsellor at the Court of Aids in Clermont-Ferrand in the Massif Central and asked him to measure the column of "mercury" at different altitudes between the town of Clermont-Ferrand and the summit of the Puy-de-Dôme at an altitude of 1,460 m. Périer hesitated at first but finally agreed. In the presence of magistrates, nobles, and

[53] nel fondo d'un pelago d'aria elementare.

clergymen, he took his first measurement on September 19, 1648, at the *Couvent des Minimes* in the city, 395 m above sea level. He climbed the mountain with a few witnesses, taking with him a glass tube, a flask, and some mercury. At the top of the Puy de Dôme, he found that the height of the column of mercury was only "23 inches and 2 lines"[54]. To make sure it was correct, he repeated his measurement five times, sometimes inside a small chapel, and sometimes outside. The values he observed were compared with measurements taken by Father Chastin who had stayed at the Couvent des Minimes, "500 fathoms"[55] below, and had an identical instrument at his disposal. Chastin measured a value of "26 inches and 3.5 lines". This second instrument was used to highlight possible variations in pressure during the course of the day. The difference in pressure expressed by the difference in height of the two columns of "mercury" was therefore "3 inches 1.5 lines", or about 9 cm. It's clear that the weight of air decreases as one rises in the atmosphere. Pascal's account of these measurements was published in 1648 in his *Récit de la grande expérience de l'équilibre des liqueurs*[56].



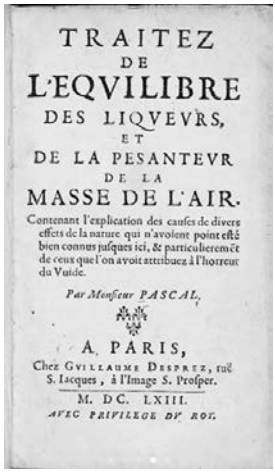

TRAITEZ
DE
L'EQVILIBRE
DES LIQVEVRS,
ET
DE LA PESANTEVR
DE LA
MASSE DE L'AIR.
Contenant l'explication des causes de divers effets de la nature qui n'avoient point esté bien connus jusques ici, & particulierement de ceux que l'on avoit attribuez à l'horreur du Vuide.
Par Monsieur PASCAL.
A PARIS,
Chez Guillaume Desprez, ruë S. Iacques, à l'Image S. Prosper.
M. DC. LXIII.
AVEC PRIVILEGE DV ROY.

Figure 2.5: Left: Measurement of atmospheric pressure by Florin Périer on the Puy-de-Dôme near Clermont-Ferrand. Source: *Les merveilles de la sciences ou Description populaire des inventions modernes* (Volume 1), published in 1867. Right: Blaise Pascal's book on the equilibrium of liquors and the gravity of the air mass, published with the King's privilege in 1663.

[54] Unit of length in the King of France system. 1 inch = 2.722 cm and 1 line = 2.268 mm or 1/12 of an inch.

[55] 1 fathom = 6 feet (approx. 1.8 m).

[56] Account of the great experiment in liquor balance.

The Elastic Air of Boyle and Mariotte

On April 27, 1661, the English physician Henry Power (1623-1668) and the mathematician and astronomer Richard Towneley (1629-1707) also decided to measure air pressure as a function of altitude. To carry out their project, they took a Torricelli tube to Pendle Hill, a small mountain 557 m above sea level in Lancashire. The measurements they took and the resulting analyses allowed them to conclude that air is "elastic", i.e., that there is a relationship between air pressure and density. They showed that the volume of a given amount of gas varies as the inverse of its pressure. Power and Towneley were about to publish their results, but in the winter of 1661-1662, they decided to send their manuscript in advance to the Anglo-Irish chemist, the aristocrat (son of the Earl of Cork) Robert Boyle, so that he could share his views with them.

Boyle, who had access to pumps built in the late 1650s by his assistant Robert Hooke (1635-1703), had conducted experiments on the properties of gases. He confirmed the results obtained by von Guericke in Magdeburg and showed that when some of the air is removed from a hermetically sealed enclosure, the remaining air is distributed throughout the enclosure, albeit at a reduced pressure. This "push back" of residual air was likened by Boyle to the behavior of a "spring", a term that appears explicitly in the subtitle of his work published in 1660. Air is clearly an elastic medium.

The book of Power and Towneley was not published until 1663, under the title *Experimental Philosophy*. Meanwhile, Boyle had taken the initiative to publish the important discovery of the two scientists under his own name, albeit with a discreet reference to what he called Towneley's "hypothesis". Perhaps because he was a natural philosopher and theologian recognized by the English aristocracy and fully committed to the Anglican Church, Boyle thought it preferable that the new law of physics bear his name. Because of their membership in the minority Roman Catholic Church in Great Britain, Power, and Towneley were very isolated from the scientific and political networks of the day, including the Royal Society. Although he appropriated the results of his two colleagues, Boyle is undoubtedly one of the founders of modern chemistry and a defender of the scientific method. He rejected Aristotle's four elements and introduced the concept of chemical elements[57]. In his 1661 book, *The Skeptical Chymist,* he wrote

> " I now mean by Elements, as those Chymists that speak plainest do by their Principles, certain Primitive and Simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the Ingredients of all those call'd perfectly mixed Bodies are immediately compounded, and into which they are ultimately resolved."

In his Treatise on Optics, published in 1720, he explained the cohesion of bodies: the particles that make up matter would be attracted to each other by a force that, in direct contact, would be extremely powerful: at short distances, it would

[57] Today, a chemical element is defined as a substance that cannot be chemically broken down into simpler substances.

produce chemical operations, but at long distances, it would have no perceptible effects. In a way, Boyle is close to the atomistic current of thought introduced in antiquity by the Greek philosophers Leucippus (5th century CE), Democritus (460-370 CE), and Epicurus (341-270 CE), as well as the Latin philosopher Lucretius[58] (approximately 94-54 CE). These philosophers, who opposed Aristotle's vision, proposed that matter (including the human soul) is composed of atoms and the void. In the nineteenth century, this view was taken up and developed by John Dalton under the name of atomic theory.

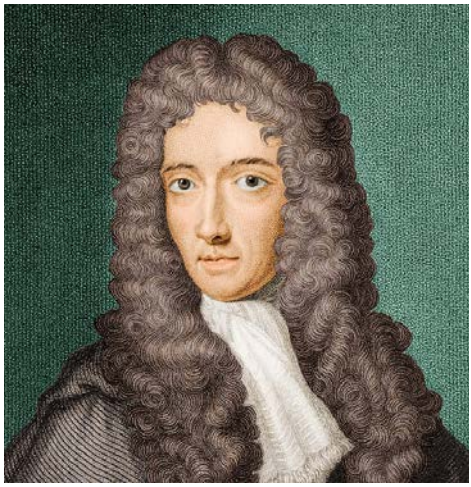


FIGURE 2.6: Robert Boyle.

Robert Boyle distanced himself from alchemy, the dominant doctrine of the day. He introduced the first concepts that would form the basis of modern chemistry and helped found the Philosophical College, the forerunner of the Royal Society.

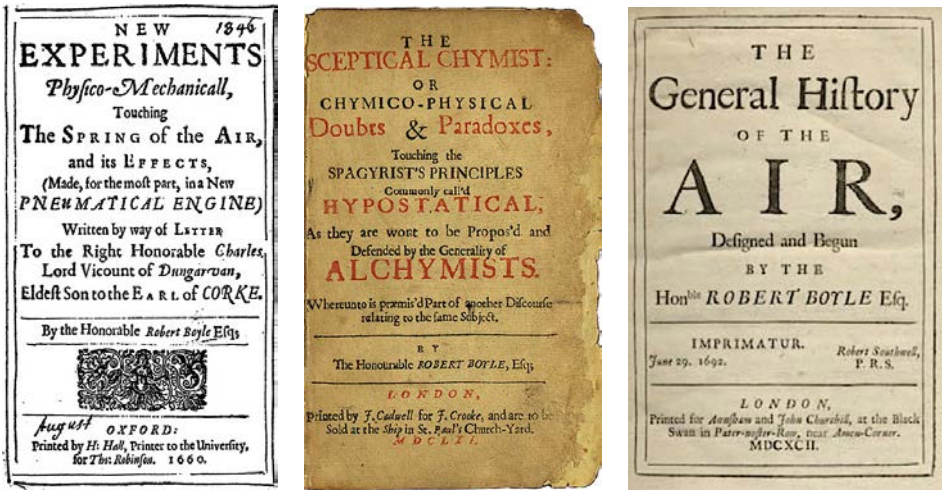


FIGURE 2.7: Three books published by Robert Boyle: Left: *New Experiments Physico-Mechanicall Touching the Spring of the Air and its Effects* (Made for the most part in a New Pneumatical engine) Written by way of Letter to the Right Honorable Charles Lord Vicount of Dungarvan, Eldest Son of the Earl of Corke. By the Honorable Robert Boyle, Efq ; Oxford, 1660. Middle: *The Sceptical Chymist*: or Chymico-Physical Doubts & Paradoxes, touching the Spagyrist's Principles commonly call'd hypostatical, As they are wont to be Propos'd and Defended by the Generality of Alchymists. Whereunto is præmis'd Part of another Difcourfe relating to the fame Subject, 1661. Right: *The General History of the Air*, 1692.

[58] The nature of air.

In France, Abbé Edme Mariotte (~1620-1684) published an essay in 1676 entitled *De la nature de l'air*. This French physicist and botanist, known for his work on the elasticity of air and one of the first members of the Académie des Sciences in Paris, proposed that Torricelli's tube be called a "barometer", which the Académie accepted. He added that the law attributed to Boyle was only correct if the air temperature remained unchanged. While Anglo-Saxon countries still refer to Boyle's law today[59] Southern European countries prefer to call it "Boyle-Mariotte's law" and, in France, as "Mariotte's law".

Decisive advances in the physical properties of air were made in the seventeenth century. We now know that the weight of air is finite. An important question remained: is the atmosphere a layer of finite vertical dimension, like the layer of water that makes up the ocean, or does it extend infinitely into space? It was therefore essential to continue to measure pressure and other atmospheric variables at higher altitudes. But how could one probe the atmosphere at altitudes previously inaccessible to humans?

Balloon Ascents and the Law of Perfect Gases

It wasn't until the 18th century that new means of reaching higher altitudes in the atmosphere were developed: kites, balloons, and then hot-air balloons. After a first attempt in Annonay, Ardèche, on December 14, 1782, in which a balloon inflated with hot air reached a height of 400 meters, two French industrialists, brothers Joseph-Michel Montgolfier (1740-1810) and Jacques-Etienne Montgolfier (1745-1799), repeated their experiment on June 4, 1783, in the Vivarais region of southeastern France. This time, the balloon reached an altitude of about 1,000 meters before landing 10 minutes later, two kilometers from the launch site. A few weeks later, on August 27, 1783, French physicist Jacques Alexandre César Charles (1746-1823), assisted by two brothers, Anne-Jean Robert (1758-1820) and Nicolas-Louis Robert (1760-1820), launched the first hydrogen-filled balloon from the Champ de Mars in Paris. The upward force of the balloon was far superior to that of hot air balloons. The balloon headed north before landing in the village of Gonesse, where the locals, seeing a flying object for the first time, panicked and destroyed the remains of the balloon, believing it to be cursed.

Intense competition arose between the promoters of hot air balloons[60] and those of the hydrogen-filled Charlières[61], especially since the Montgolfier brothers' initiative was supported by King Louis XVI, while Charles' initiative was not. On September 19, 1783, another hot air balloon was launched, this time from Versailles in the presence of the King. The vehicle carried

[59] For a given quantity of a so-called "perfect" gas maintained at a constant temperature, Boyle-Mariotte's law states that a decrease in the volume of a gas leads to an increase in its pressure. Conversely, a decrease in the gas's pressure results in an increase in its volume. The product of pressure and gas volume is constant.

[60] Hot-air balloon named after the Montgolfier brothers.

[61] Hydrogen balloon named after physicist Jacques Charles.

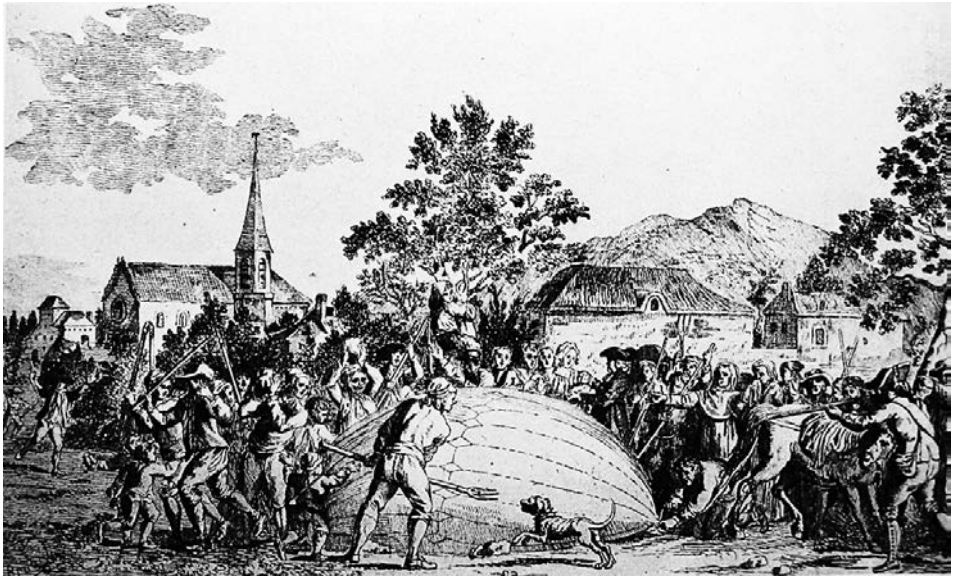


FIGURE 2.8: The balloon of Jacques Charles and the brothers Robert lands in the village of Gonesse near Paris. It is attacked by villagers who are frightened by the object falling from the sky and fear a curse on their village.

three animals in a wicker basket: a sheep, a duck, and a rooster. The balloon only reached an altitude of 500 meters, and the animals were luckily rescued unharmed. A month later, on October 19, 1783, a captive hot air balloon (held to the ground by a cable) rose to a height of 81 meters above the Faubourg Saint-Antoine in Paris. The first free manned flight took place on November 21 of the same year. The balloon, which this time weighed 850 kg, rose above the Château de la Muette in the 16th arrondissement of Paris, reaching an altitude of 1,000 meters as it flew over the Parc des Tuileries, before landing on the Butte-aux-Cailles in the 13th arrondissement. It carried the first two aeronauts in history, François Laurent, Marquis d'Arlandes (1742-1809), and Jean-François Pilâtre de Rozier (1754-1785), despite the reluctance of the King, who would have preferred to grant a royal pardon to two condemned men who volunteered for the climb. On June 15, 1785, Pilâtre de Rozier died by accident near Boulogne-sur-Mer at the age of 31 while attempting to cross the English Channel in a hot air balloon.

For his part, Charles decided to build a hydrogen-filled balloon capable of carrying two passengers. On December 1, 1783, accompanied by his co-pilot, the engineer Nicolas-Louis Robert, he took off from the Jardin des Tuileries in Paris. The two men took a barometer and a thermometer with them to make the first meteorological measurements at altitude. The flight lasted 2 hours and 5 minutes and they landed at Nesles-la-Vallée. Elected a member of the Paris Academy of Sciences in 1795, Charles continued his research into the physical properties of air: he found that the volume of air contained in a balloon increased when it was heated. He deduced that, at constant pressure, the volume occupied



FIGURE 2.9: Postcard showing the ascent in a hydrogen-filled balloon (left) that carried Jacques Charles (right) and Nicolas-Louis Robert over the Paris region in 1783.

by a gas is directly proportional to its absolute temperature[62]. However, he did not publish his results, and it was not until 1802 that the chemist and physicist Joseph Louis Gay-Lussac (1778-1850) referred to his work.

Other atmospheric ascents were organized in the following years. In 1784, for example, the American physician John Jeffries (1744-1819) made meteorological observations from a balloon over London. And in 1804, at the suggestion of the chemists Claude Louis Berthollet (1748-1822) and Pierre-Simon Marquis de Laplace (1749-1827), Gay-Lussac, accompanied by the physicist Jean-Baptiste Biot (1774-1862), made several ascents in a hot-air balloon. Their goal was to measure air pressure, temperature, and the Earth's magnetic field. During one of these ascents in 1804, the two aeronauts reached an altitude of 7,016 meters and brought back air samples for analysis in the laboratory. These measurements led Gay-Lussac to claim that for a given amount of gas contained in a constant volume, the gas pressure increases proportionally to the absolute temperature[63]. This new law is of great importance for our understanding of meteorological phenomena.

In 1801, John Dalton (1766-1844) showed that the pressure of a gas mixture is equal to the sum of the partial pressures of its components. The French

[62] At constant pressure, Charles' law can be written as follows: $V_1/T_1 = V_2/T_2$ if V and T represent the volume and temperature of a given quantity of gas for two conditions 1 and 2.

[63] Gay-Lussac, J.L., Recherches sur la dilatation des gaz et des vapeurs, *Annales de Chimie, XLIII*, 137, 1802. Gay-Lussac's law, which is now explained by the kinetic theory of gases, can be written as follows: For a given quantity of gas contained in a constant volume, we have $p_1/T_1 = p_2/T_2$, if p and T represent the pressure and temperature of the two conditions 1 and 2.

physicist Émile Amagat (1841-1915) added that the volume of a gaseous mixture is equal to the sum of the volumes of the various gases that make up the mixture. In 1834, the French engineer Émile Clapeyron (1799-1864) combined the laws of Charles, Boyle and Mariotte, Gay-Lussac, Dalton, and Amagat to form the famous law of perfect gas[64] which links pressure, volume, and temperature of gases. Today, this law is rigorously established by the kinetic theory of gases.

In his book *Exposition du système du monde*[65], published in Paris in the fourth year of the French Republic, Pierre-Simon de Laplace summarized what was known at the end of the eighteenth century and showed that air density decreases geometrically with altitude.

> "An elastic fluid, rare and transparent, envelops the Earth, and rises to great heights; it weighs like all bodies, and its weight balances that of mercury in the barometer. At the temperature of melting ice, and at the average height of the barometer at sea level, a height of about two and a third feet, the weight of air is equal to that of a similar volume of mercury in the ratio of unity to 10,320. Thus, at this temperature, to lower the barometer by one hundredth of a foot, when its height is two and a third feet, it is sufficient to rise by 103.20 feet, and if the density of the atmosphere were the same everywhere, its height would be 24,080 feet[66]. But air is very nearly compressible because of the weights with which it is loaded; hence it follows that, at equal temperatures, its density is proportional to the height of the barometer; its lower layers are therefore denser than the upper layers, whose weight compresses them; they become rarer and rarer as we rise in the atmosphere, and if their temperature were the same, a very simple calculation shows us that as their height increases in arithmetic progression, their density would decrease in geometric progression."

Further advances were made in the 19th century. Between 1862 and 1866, English meteorologist James Glaisher (1809-1903), who worked at the Royal Observatory in Greenwich, and his co-pilot Henry Tracey Coxwell (1819-1900) made several balloon flights to measure air pressure, temperature, and humidity. On September 5, 1862, the two men decided to explore the upper layers of the atmosphere. During their ascent, Glaisher regularly observed the atmospheric pressure, which allowed him to estimate the balloon's altitude. He also measured the relative humidity of the air as a function of altitude. At 8,800 meters (the

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64 $pV = nRT$ where p is the pressure (Pa), V the volume of the gas (m^3), n the quantity of substance (mol), T the absolute temperature (Kelvin) and R the universal gas constant (8.314 J K^{-1} mol^{-1}).

65 Laplace, Pierre-Simon, Exposition du système du monde (Presentation of the World system), Imprimerie du Cercle-Social, Paris, An IV (1795-1796). Third edition published in 1808 by Courcier, Imprimeur-Librairie pour les Mathématiques, Paris.

66 In the third edition of his work, published in 1801, Laplace adopted metric units in his text. He writes: "The weight of air is equal to that of a similar volume of mercury, in the ratio of unity to 10,477.9; from which it follows that by rising from 10,4779 m, the height of the barometer would fall by about 1 mm, and that if the density of the atmosphere were the same everywhere, its height would be 7,963 m".

last pressure reading taken), Glaisher, running out of oxygen, lost consciousness. Air had become so scarce that one of the pigeons the crew had brought along died of asphyxiation. Coxwell, who had lost all feeling in his hands and feet found it extremely difficult to stop the balloon's ascent. It is estimated that the balloon reached an altitude of 35,000 feet (11,000 meters) before Coxwell was able to open the balloon valve by using his teeth to operate the rope that opened it. At this point, Coxwell also lost consciousness. Fortunately, the balloon descended 6,000 meters in 15 minutes. The two aeronauts landed safely about ten kilometers from their launch site.



FIGURE 2.10: Glaisher and Coxwell's dramatic balloon ascent in 1862.

In the following years, Gustave Hermite (1863-1914) and Georges Besançon (1866-1934) carried out systematic measurements of temperature and pressure at altitude in the Paris region. They regularly launched small oiled-paper balloons, inflated with hydrogen, from which a *meteograph* was suspended to record pressure and temperature during the flight. The instrument, to which a postcard was attached for return to the experimenters, was recovered, and the data analyzed. In 1893, Hermite and Besançon decided to build a larger rubber balloon capable of reaching higher altitudes. This unmanned balloon, launched on March 21 of that year, reached an altitude of 16,000 m, and the onboard thermograph showed that above a height of about 13.5 km, the temperature no longer decreased with altitude. Similar balloon-sonde measurements between 1899 and 1903 led the meteorologists Léon Philippe Teisserenc de Bort (1855-1913) at the Trappes Observatory in the Paris region and Richard Assmann (1845-1918) at the Lindenberg Observatory in Prussia to announce almost simultaneously in 1905 the existence of a stable, stratified atmospheric layer in which the temperature no longer decreased or even slightly increased with altitude. Teisserenc de Bort named this layer the stratosphere. Today we know that the stratosphere extends to an altitude of about 50 km.

The Vertical Structure of the Atmosphere

Since then, daily measurements of air temperature and humidity have been made under the auspices of meteorological centers. The first radio meteograph was invented in 1927 by the Russian meteorologist Pavel Alexandrovich

Moltchanoff (1893-1941), who began taking soundings in the stratosphere in 1930. Radiosondes were also developed by Robert Bureau (1892-1965) and Pierre Idrac (1885-1935) in France, Vilho Väïsälä (1889-1969) in Finland, and Jules Jaumotte[67] (1887-1940) in Belgium. Today, the development of space technologies, and in particular remote sensing, means that temperature and water vapor can be measured continuously from satellites. These global-scale observations are particularly useful for initializing weather prediction models.

Thanks to measurements made since the nineteenth century, we now have a good understanding of the vertical structure of the atmosphere: atmospheric pressure, which averages 1013 hectopascals (hPa) at sea level (equivalent to 76 cm of mercury), decreases almost exponentially with altitude. It drops to 540 hPa at an altitude of 5 km, 264 hPa at 10 km, 55 hPa at 20 km, and 12 hPa at 30 km. The average temperature of the Earth is about 15 °C at ground level but decreases in the *troposphere* by about 6.5 °C per km, reaching a minimum of about -50 °C *at the tropopause*, the upper limit of this layer. The tropopause is located at about 18 km in the tropics, 12 km in the mid-latitudes, and nearly

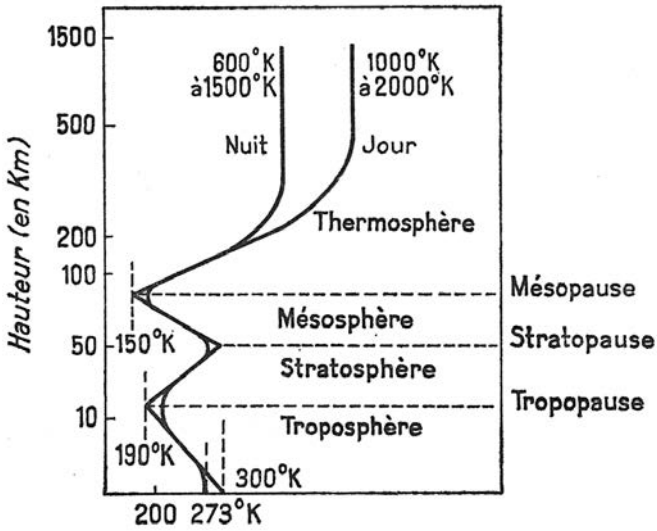


FIGURE 2.11: Vertical temperature structure in the Earth's atmosphere from ground level to 1500 km altitude, established in the 1960s. Source: Delobeau, F., L'environnement de la Terre, Presses Universitaires de France, 1967. Curve based on work by M. Nicolet in the nineteen-sixties.

[67] This military aviator, a specialist in aerial photography, took part in military operations during the First World War. He was appointed director of the Royal Belgian Meteorological Institute in 1919. After the invasion of German troops on June 10, 1940, the Meteorological Institute accompanied the withdrawal of Belgian troops to the coastal region near France. During a bombardment in the small town of Saint Idesbald on June 1, 1940, Jules Jaumotte's eldest son Jacques, 11 years old, was killed instantly and the director of the Meteorological Institute was seriously wounded. He was taken to Uccle where he died on July 1, 1940.

8 km in the polar regions. It is in the troposphere that the most important meteorological phenomena occur (synoptic systems, clouds, precipitation, etc.). Above the tropopause is the *stratosphere*, a dynamically stable region rich in ozone. Here, the average temperature increases with altitude up to the level of the *stratopause*, 50 km above sea level. Between 50 and 90 km, the average temperature decreases, and the corresponding atmospheric layer is called the *mesosphere*, with the *mesopause* at about 80 km as its upper limit. Finally, above 90 km, under the influence of very intense solar radiation, the temperature increases significantly with altitude, and the corresponding layer is called *the thermosphere*. The temperature of this atmospheric region varies considerably according to the intensity of the radiation emitted by the Sun, especially in the ultraviolet. Specifically, solar activity varies with an 11-year cycle and its effect is very noticeable on the physical and chemical quantities that characterize the upper atmosphere.

Box 2.3. Atmospheric Pressure as a Function of Altitude

Pressure measurements taken at altitude, thanks to balloon ascents, have shown that atmospheric pressure decreases almost exponentially with altitude. The law of decreasing air pressure can be established by writing that there is an equilibrium between the weight of the air and the vertical pressure gradient. If ρ represents the specific mass of air (kg per m^3), p its pressure (Newton per m^2), g the acceleration due to gravity (9.81 m per s^2) and z the altitude (m), we write:

$$\frac{dp}{dz} = -\rho g$$

The pressure and specific mass of air are linked by the perfect gas equation:

$$p = \rho R T$$

where $R = k/m$ if m (kg) represents the average mass of air particles (molecules and atoms) and $k = 1.38\ 10^{-23}$ Joules per Kelvin is Boltzmann's constant. Eliminating ρ we find that

$$\frac{dp}{dz} = -\frac{p}{H}$$

if

$$H = \frac{RT}{g}$$

which is called the height scale, represents a length that determines the rate at which pressure decreases with altitude. The value of H is of the order of 8 km in the lower layers of the atmosphere, but increases considerably with altitude under the effect of the gradual decrease in the average mass of air

particles and the increase in temperature. If we assume that the scale height is constant in the lower layers of the atmosphere, we can deduce from the above equations that pressure decreases exponentially with altitude:

$$p(z) = p(0)e^{-z/H}$$

where $p(0)$ is the pressure at altitude $z = 0$.

3
Air or "Airs"?

Until the sixteenth century, our understanding of natural phenomena was dominated by scholasticism, the medieval philosophical movement that combined the Greek thought of Aristotle with the Christian theology inherited from the Church Fathers. Air, one of the four basic elements of the universe, was considered a homogeneous, inert substance with little influence on living things. In the early Renaissance, however, this perspective changed. Air, which plays a critical role in the processes of combustion and respiration, appeared to be composed of several elements with different physical and chemical properties. With the advent of a new discipline, *pneumatic chemistry*, a systematic study of the chemical composition of air began to take shape. Based largely on experimental work, this science, which describes chemical transformations within gaseous mixtures, attracted the greatest minds in Europe, including Robert Boyle, Stephen Hales, John Dalton, Joseph Black, Henry Cavendish, Daniel Rutherford, Joseph Priestley, Carl Scheele, and Antoine Lavoisier. Lavoisier showed that the various "airs" isolated in the seventeenth and eighteenth centuries could not be separated. The eminent French chemist was the spokesman of a scientific revolution that gave rise to a rational approach well described in his *Traité élémentaire de chimie*, published in 1789.

Scientific revolutions often begin with the invention of a new system of measurement. Such was the case with the study of the composition of air. In 1727, the Reverend Stephen Hales (1674-1761), a British theologian, botanist, and chemist, developed a simple instrument, the *pneumatic vat*, which allowed scientists of the time to collect and isolate different "airs" in order to study their chemical properties. The apparatus was simple: it consisted of a tank filled with water and a flask, also filled with water, that was inverted so that its opening was immersed in the liquid of the tank. The gas to be analyzed was produced by a chemical reaction outside the apparatus and then introduced into the flask through a flexible tube; the gas bubbles rose through the water and accumulated at the top of the flask, causing the liquid level in the flask to drop due to the pressure of the now isolated gas.

The pneumatic tank was the precursor of *the eudiometer*, an instrument used for several centuries to measure changes in the volume of a gas resulting from a chemical reaction or combustion process (Box 3.1). This instrument, very popular with chemists of the time, had an elongated shape reminiscent of

a thermometer or barometer. It was designed to measure the purity of the air, called the "goodness of the air", and specifically to determine the amount of "vital air", i.e. the oxygen present in "ordinary air".

These early instruments allowed the identification of several "airs", including "fixed air" (carbon dioxide) by Joseph Black in 1755, "flammable air" (hydrogen) by Henry Cavendish in 1766, "harmful air" (nitrogen) by Daniel Rutherford in 1972, "nitrous air" (nitrogen oxide) by Joseph Priestley in 1772, and "vital air" or "dephlogisticated air" (oxygen) by Carl Scheele, Joseph Priestley, and Antoine Lavoisier between 1771 and 1777. At the same time, Alessandro Volta built an eudiometer from a so-called "electro-phlogopneumatic pistol"[68], which allowed him to study the explosive properties of the "flammable air of swamps" (methane)[69].

Pneumatic chemistry mobilized the followers of natural philosophy, especially in Britain and France, for almost two centuries. It thus preceded the chemical revolution initiated by Lavoisier just as the French Revolution was getting underway. But it was in the suburbs of Brussels that an important discovery was made in the first half of the seventeenth century.

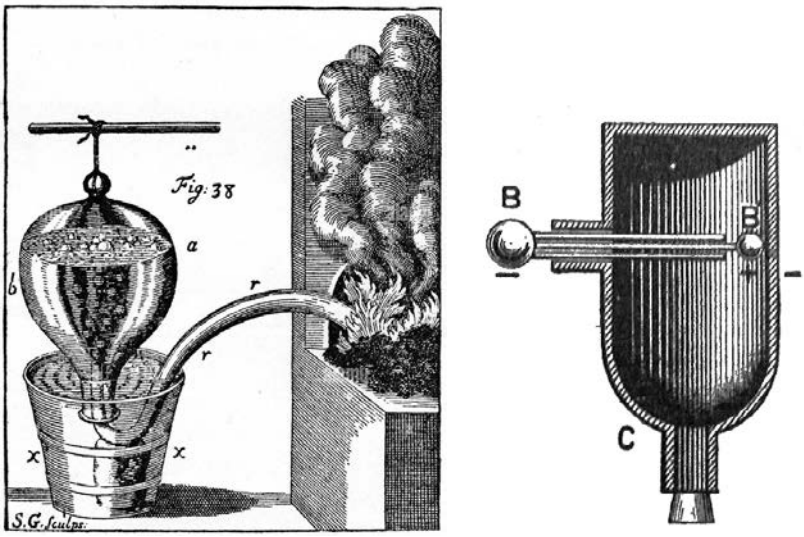


FIGURE 3.1: Left: Stephen Hales's pneumatic tank. Right: Volta's pistol. The spark that generates the explosion of the "swamp air" shoots up between the ball B' and the metal wall C of the gun. The explosion ejects the cork blocking the opening near point C. Source: Pierre Larousse, Grand Dictionnaire universel du XIX^{e} siècle en 15 volumes (1868-1877).

[68] Metal vase closed with a cork that can be filled with a detonating gas mixture. Volta's pistol fired projectiles through the ignition of methane with an electric spark.

[69] *Aria infiammabile native delle paludi.*

The Galileo of Brabant

Johann Baptista van Helmont de Brabant, Seigneur de Mérode, Royenboch, Oorschot et Pellines, was born in Brussels, probably on January 12, 1579, or perhaps on the same date in 1577. A member of a noble, Catholic Brabant family, he studied philosophy at the University of the Duchy of Brabant (later the Catholic University of Louvain) and theology at the new Jesuit college in Louvain. This college was founded despite opposition from the king and Pope Clement VIII. Van Helmont studied geometry, algebra, and astronomy. He took advantage of his stay to read the mystical texts of Christianity. He then turned to medicine, graduating in 1599, and immediately began practicing his art of healing at a time when Europe was in the grip of the plague epidemic of 1605. He traveled to several European countries, including Switzerland, Italy, France, and England, before returning to Belgium in 1606. He declined an invitation from the Jesuits to join their order, preferring instead to marry Marguerite van Ranst, also from a noble family, in 1609. The couple settled in Vilvoorde, a small town near Brussels. They had four daughters and a son.

Van Helmont's thought was somewhere between mysticism, metaphysics, alchemy, astrology, and cosmology, but at the same time, this inquisitive man was open to progress and turned to modern science, especially chemistry, which he saw as the driving force of life. However, he did not separate scientific and spiritual research. He was attracted to the theories of the Swiss physician *Paracelsus* (real name Philippus Theophrastus Aureolus Bombast von Hohenheim, 1493-1541), who believed that chemistry played a fundamental role in the behavior of the human body. He advocated the use of chemical remedies to treat a variety of ailments, challenging the traditional methods of Galenic medicine[70] of the time. Paracelsus believed that physicians should have an excellent knowledge of the natural sciences, especially chemistry. He was convinced that all disease is caused by a combination of three principles (which he called the *tria prima*): salt, sulfur, and mercury. Curing disease therefore, required a clear understanding of the role of these *tria prima*. Van Helmont, seduced by Paracelsus[71], is often considered the founder of *iatrochemistry*, or medical chemistry, and thus one of the earliest proponents of the pharmacopeia. Brought up in the tradition of the Greek philosophers, he rejected Aristotle's view of the world in terms of the four elements mentioned in the previous chapters: for him, only air and water were the fundamental elements: air would contain various substances that he considered inert, while water would be subject to chemical transformations. This view is consistent with the Genesis texts in the Bible.

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[70] A medical system developed during the Middle Ages and inspired by the ancient physician Galen of Pergamon (129-216) and his theory of the four humors. This was based on the four fundamental elements of the universe: air, fire, water and Earth, and four qualities: hot or cold, dry or wet.

[71] Interestingly, Paracelsus suggested that thunder and lightning resulted from the explosion of "*aerial nitre*" present in the air.

In his laboratory, where he carefully analyzed the transformations of matter, van Helmont noted that the combustion of sixty-two pounds of coal produced just under one pound of ash, and that the difference in mass disappeared in a form "more subtle or fine than a vapor, mist, or distilled oily substance, though very often thicker than air". The physician-chemist concluded that matter is transformed into a wild *ghost*, which he described by the Flemish name "*geest*", a name that seems to be the origin of the French word *"gaz"* or the English word "*gas*". In a Flemish text published in 1659, van Helmont wrote: *Gas veel subtijlder is dan eenigen damp* (Gas is much more subtle than any steam). However, the exact etymology of the name "gas" remains uncertain, since some consider it more likely that the origin of this term is linked to the Greek name χα'ος (khaos, confused mass). In any case, in addition to the burning of coal, van Helmont identified several other sources (including fermentation and wood burning) of the substance he called "*spiritus sylvestris*" (*spirit of the wild*), which we know today as "carbon dioxide" or "carbon monoxide". The Brabant scholar had just founded pneumatic chemistry, which, as we have seen, was to dominate thought for several centuries. For the first time, the air seemed to contain various compounds, in particular "gas sylvestre", about which little was known except that it was produced by combustion.

Johan van Helmont performed another puzzling experiment: he lit a candle placed vertically in a bowl of water and covered the candle with an upside-down glass, the rim of which was immersed in the water in the bowl. After a few seconds, the candle went out and the water seemed to be sucked back into the glass. Van Helmont concluded that some of the matter in the air must have been destroyed by the fire, and that the water in the glass rises to compensate for the matter that has disappeared. This explanation is incorrect, but as we will



FIGURE 3.2: Left: Johan Baptista van Helmont, the Flemish physician and chemist who discovered the existence of "gas sylvestre" in the air. Right: Cover of the book presenting van Helmont's works, published in 1671.

see later, it would take 150 years for chemists to correctly interpret the results of this experiment. In any case, the candle flame changed the properties of the air trapped in the glass. There was probably not a single air, but different "airs".

Johan van Helmont was considered a rebel by the scholars of his time. He came into conflict with the Catholic Church over his treatise *De magnetica vulnerum curatione* [On the Magnetic Healing of Wounds], published in Paris in 1621. The denunciation of the work to the Spanish Inquisition by Father Jean Roberti (1569-1651), a Luxembourg Jesuit born in Saint-Hubert and rector of the Collège de Padeborn, led to the physician-chemist's condemnation in 1625 for heresy, arrogance, and being too close to the Protestant doctrines of Luther and Calvin. Initially, van Helmont avoided imprisonment, but by the time Galileo was condemned in 1634, religious persecution was back in full swing. He was first briefly imprisoned in a Franciscan monastery in Brussels, then placed under house arrest until 1636. His writings, published between 1599 and 1634, were confiscated and his teaching at the Catholic University of Louvain was suspended because the Church claimed that they were influenced by the ideas of Paracelsus. In 1642, however, van Helmont received the *imprimatur* of the Church to publish his work on fever, two years before his death in 1644. The other publications of this "Brabant Galileo" were rehabilitated by the Catholic Church in 1646 and published after his death thanks to his son.

Fixed Air

Hales. While the discovery of "gas sylvestre" can be attributed to Johan van Helmont, the 18th century brought new insights into the role of atmospheric gases and their relationship to the functioning of living organisms. The English clergyman Stephen Hales (1677-1761), a member of the Royal Society and famous for the first measurements of human blood pressure, contributed to the development of pneumatic chemistry. The scholar who would become rector of Farringdon in Hampshire and Anglican minister of Teddington in Middlesex defined his research method for studying the physical properties of air:

> "And since we are assured that the all-wise Creator has observed the most exact proportions of number, weight and measure in the make of all things, the most likely way, therefore, to get any insight into the nature of these parts of the creation which come within our observation must in all reason to be number, weight and measure."

Reverend Hales, interested in botany, noticed that plants get a significant portion of their nutrition from the air, probably through their leaves. He pointed out that light is a source of energy that enables plants to "ennoble" themselves; he thus introduced the notion of *photosynthesis*, that is, the development of organic matter in plants through the transformation of atmospheric gas. He believed that the common air existed in two forms: *Elastic air*, whose laws of compressibility had been demonstrated by Boyle and Mariotte, and *fixed air*, i.e., the air fixed in plants and other organic bodies. In the sixth chapter of his

book "*Vegetable Staticks*"[72] published in 1735, Hales describes what he means by *fixed air*:

> [...] "It will be seen that all bodies contain a large quantity of air; that this air is often in these bodies in a form different from that which we know; that is, in a state of *fixity* where it attracts as powerfully as it repels in its ordinary state of elasticity. [...] These mutually attractive particles *of fixed air* are [...] often expelled from dense bodies by heat or fermentation and transformed into other particles of elastic or repelling air [...] It is through this amphibious property of air, that the principal operations of nature are carried out."

Black. This work influenced the thinking of the Scottish physicist and chemist Joseph Black (1728-1799), who is often credited with rediscovering carbon dioxide, which van Helmont had identified one hundred and fifty years earlier. This man of the world was born in Bordeaux, France, where his father, originally from Belfast and descended from a Scottish family, worked as a wine merchant on the banks of the Garonne. His Scottish mother taught him to speak English. The family moved to Northern Ireland when Black was twelve. At the age of eighteen, Black began studying medicine at the University of Glasgow, where he admired the chemistry taught by Professor William Cullen (1710-1790). From 1751, he continued his studies at the University of Edinburgh and, after submitting a dissertation[73] which was a prelude to his later scientific work on alkalinity, he received his medical degree in 1754. His thesis was on the use of quicklime (CaO) as a treatment for urinary stones. However, opinion was divided as to the efficacy of this treatment, which led Black to search for an alternative substance. This led him to study the properties of *white magnesia* (*magnesia alba* or magnesium carbonate $MgCO_3$) and to discover that the calcination of this *magnesia-producing* substance (*magnesia usta* or MgO) was accompanied by weight loss[74]. The same applies to the calcination of chalk (calcium carbonate or $CaCO_3$) to produce quicklime (calcium oxide, CaO). Black explained this weight loss by noting that these chemical transformations release a gas that he called *fixed air*, a name already used by Hales. Black had just rigorously identified the gas we now call carbon dioxide. From 1756 to 1766, he was a professor of anatomy and chemistry at the University of Glasgow, before becoming a

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[72] Vegetable staticks, or An account of some statical experiments on the sap in vegetables: being an essay towards a natural history of vegetation: Also, a specimen of an attempt to analyse the air, by a great variety of chymio-statical experiments, which were read at several meetings before the Royal Society, 1727.

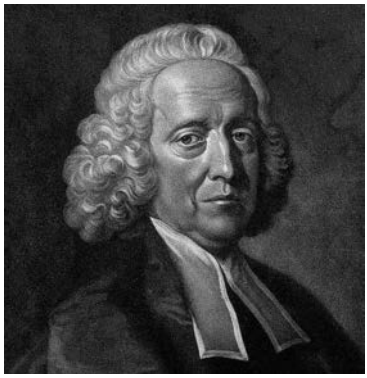
[73] Black, J., *De humore acido a cibis orto, et magnesia alba* [On acid humor from food and white magnesia], 1754.

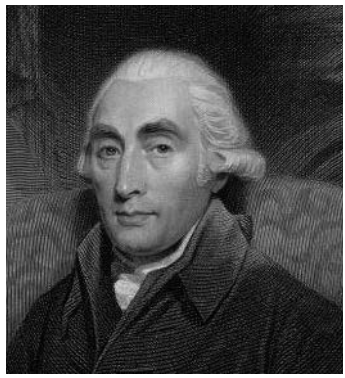
[74] The decomposition reaction of *magnesia alba* ($MgCO_3$) is as follows: $MgCO_3$ + heat $\rightarrow$ MgO + CO_2. Conversely, when MgO magnesia is brought into contact with fixed air, *magnesia alba* reforms. Black also notes that, if fixed air comes into contact with dead lime ($Ca(OH)_2$), a precipitate is formed which is calcium carbonate ($CaCO_3$). The reaction is as follows: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$. As this reaction occurs when a person blows on lime, Black deduces that the fixed air is a product of respiration.

professor of medicine and chemistry at the University of Edinburgh, where he taught for over thirty years. In 1756, he wrote[75]:

> "I have given it the name of *fixed air*, and perhaps very improperly, but I thought it better to use a name familiar in philosophy, than to invent a new name before we are better informed of the nature and properties of this substance, which will probably be the subject of my forthcoming research."

Black added that this fixed air is different from ordinary air, but that it can easily mix with the latter, even in very small quantities. Black's work has the merit of being based on systematic, quantitative measurements and allows us, for the first time, to identify a very specific gas present in the air. Despite the quality of this experimental work, dissenting voices were heard.





VEGETABLE STATICKS:
Or, An Account of some
Statical Experiments
ON THE
SAP in VEGETABLES:
Being an ESSAY towards a
Natural History of Vegetation.
Also, a SPECIMEN of
An ATTEMPT to Analyse the AIR,
By a great Variety of
CHYMIO-STATICAL EXPERIMENTS;
Which were read at several Meetings before the ROYAL SOCIETY.
By STEPH. HALES, B. D. F. R. S.
Rector of Farnham, Hampshire, and Minister of Teddington, Middlesex.
LONDON:
Printed for W. and J. INNYS, at the West End of St. Paul's and T. WOODWARD, over against St. Dunstan's Church in Fleetstreet. M, DCC, XXVII.

EXPERIMENTS
UPON
MAGNESIA ALBA, QUICK-LIME,
AND OTHER
ALCALINE SUBSTANCES;
By JOSEPH BLACK, M. D.
Professor of Chymistry in the University of Edinburgh.
To which is annexed,
An ESSAY on the COLD
Produced by EVAPORATING FLUIDS,
AND
Of some other means of producing COLD;
By WILLIAM CULLEN, M. D.
Professor of Medicine in the University of Edinburgh.
EDINBURGH:
Printed for WILLIAM CREECH, Edinburgh; and for J. MURRAY, and WALLIS and STONEHOUSE, London.
M, DCC, LXXVII.

FIGURE 3.3: Left: Stephen Hales and the cover of his book presenting his analysis of air. Source: Biodiversity Heritage Library. Right: Joseph Black and the cover of his 1756 work in which he identified carbon dioxide, which he called fixed air.

[75] Black, J. *Experiments upon magnesia alba, quick-lime, and other alkaline substances*, 1756.

For example, in a book[76] published in 1764, Johann Friedrich Meyer (1705-1765), an apothecary from Osnabrück, Germany, pointed out that, contrary to Black's claim, the calcination of calcium carbonate resulted in weight gain due to the appearance of an acid, *acidum pingue*, which gave quicklime its causticity. But this strange theory did not catch on, and Black's thesis was eventually accepted.

In 1777, the English chemist Henry Cavendish (1731-1810) demonstrated that the air exhaled by mammals was essentially *fixed air*. By dissolving alkalis in acid, he produced this gas, which he could store in bottles. This allowed him to study its physical properties.

The Phlogiston Controversy

Despite the progress made by the work of the Flemish chemist van Helmont and the Scottish chemist Black, the processes that make combustion possible were still not fully understood. Fundamental problems remained to be solved: what is the mechanism that transforms combustible matter into residues whose mass is much less than that of the fuel? What is the substance that sustains combustion? Why does combustion stop when it occurs in an enclosed space? Two very different theories were formulated, and they would clash for over a century, until at least 1770.

The first of these theories is known as *the phlogiston theory.* It states that every combustible material contains a colorless, odorless, and imponderable substance called *phlogiston*, which is released when the material is burned. The residue of combustion is a "dephlogisticated" substance. This view is consistent with Empedocles' concept of the four elements (air, Earth, water, fire): phlogiston is the substance of fire. Note that according to this hypothesis, the mass of the combustion residue must be less than that of the fuel and that the combustion process can occur regardless of the chemical composition of the surrounding air.

In the second theory, combustion results from a chemical reaction between the fuel and oxygen borrowed from the air. The oxygen is absorbed by the burning material and oxidizes it. This theory helps explain one of the shortcomings of the phlogiston theory: certain materials, such as magnesium and tin, gain weight during the calcination process. Respiration is a process similar to combustion.

The debate among natural philosophers, the various stages of which we shall trace, is instructive as to the progress of knowledge. The following account shows how a theory applicable to such fundamental processes as combustion and respiration was developed, then questioned, and finally rejected outright.

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[76] Meyer, F., *Essais sur la chimie de la chaux vive, la matière élastique et électrique, le feu et l'acide universel*, 1764.

Proponents of the Phlogiston Theory

Becher. The *phlogiston theory* was proposed in 1667 by the alchemist and physician Johann Joachim Becher (1635-1682), professor at the University of Mainz and personal physician to the elected archbishop of that German city[77]. To describe natural phenomena, Becher replaced Aristotle's four elements with the three forms of the Earth: *Terra lapidea* (solid Earth), *Terra fluida* (liquid Earth), and *Terra pinguis* (oily Earth). The latter, which is combustible, loses its "igneous principle" by the flame produced during the combustion and dissolves in the surrounding air. The residue, no longer combustible, forms a "dephlogisticated body".

Stahl. This hypothesis was taken up and expanded by another chemist, Georg Ernst Stahl (1659-1734), physician to the King of Prussia, Frederick William I, who taught at the University of Jena and later at Halle. In 1703, he replaced the term *terra pinguis* with the word *phlogistics*, borrowed from the Greek term φλογιστον (to burn), which in turn is related to the noun φλοξ (phlogos, flame). *Phlogiston* is therefore the "fire substance," present in large quantities in easily combustible materials such as wood, coal, and metal. Combustion is therefore seen as a *dephlogistication* process that stops when the air is saturated with phlogiston, or when all the phlogiston contained in the burning material has been dissipated. For example, when metal is calcined, phlogiston escapes into the air; the residue is called "lime" but is an oxide of the metal[78]. Phlogiston is also emitted by respiration but is reabsorbed by plants, thus preventing its accumulation in the atmosphere.

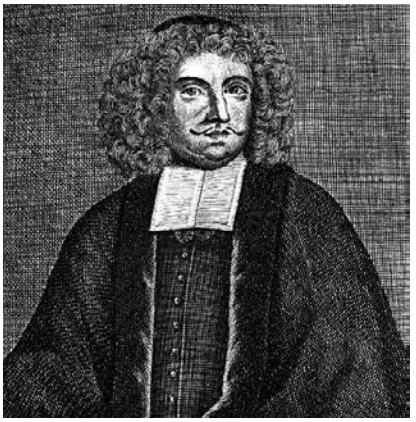


FIGURE 3.4: Johann Becher. Source: Alex Bickle's photo album.

From this concept, Stahl attempted to develop a general theory of phlogiston to unify the description of chemical processes. This theory, which brought its author immense fame and dominated thinking in Europe for the first three-quarters of the 18th century, was adopted in France, notably by Guillaume-François Rouelle (1703-1770), the king's apothecary and one of Antoine-Laurent de Lavoisier's teachers. Rouelle considered phlogiston to be the "elemental fire" rather than the fuel that sustains the flame. The theory also had great success in Germany, thanks to the apothecary Caspar Neumann (1683-1737), a member of London's Royal Society since 1726, and Stahl's student Heinrich Pott (1692-1777). Didn't the German philosopher Immanuel Kant (1724-1804) say that the discovery of phlogiston was as important as the one that led to Isaac Newton's law of falling bodies?

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[77] The Archbishop-Elector of Mainz was *Primas Germaniae* and the Pope's representative north of the Alps.

[78] Lime is Latin for *calx*, so the word calcination refers to the production of what used to be called "lime". Today, this name is reserved for calcium oxide (CaO).

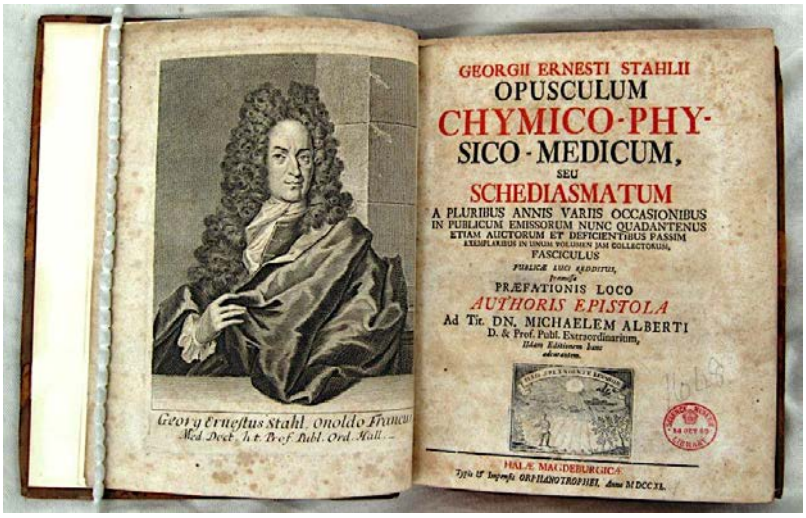


FIGURE 3.5: Treatise on chemistry-physics-medicine by Georg Ernst Stahl, published in Latin.

Rutherford. The phlogiston theory had a strong advocate in Daniel Rutherford (1749-1819), a Scottish physician, chemist, and biologist. A student of Joseph Black, Rutherford received his M.D. from the University of Edinburgh in 1772 and went on to become a Fellow of the Royal Society of Edinburgh and Professor of Botany at the University of Edinburgh. To identify the gases that make up air, he repeated the experiment of the Flemish chemist van Helmont. After eliminating the *dephlogisticated gas* (oxygen) needed for combustion and respiration by lighting a candle in a closed container (until the flame was extinguished) or by confining an unfortunate mouse (until it suffocated), he produced *the fixed air* (CO_2) that Black had identified. This gas was also eliminated by reaction with a caustic alkali. The highly inert gaseous residue, which Rutherford called *noxious air* in 1772 and which we now call *nitrogen* (N_2), cannot sustain combustion or respiration[79]. Referring to the phlogiston theory of the time, the Edinburgh chemist explained his discovery by stating that bodies subjected to combustion emit phlogiston, which combines with the surrounding air and changes its properties. Thus, Rutherford's nitrogen is considered *phlogisticated air*, even though it is not combustible.

Cavendish. Henry Cavendish[80] (1731-1810), second son of Lord Charles Cavendish, himself the third son of the Duke of Devonshire, also belonged to the group of "pneumatic chemists" who were interested in the chemical composition of air and initially believed in the existence of phlogiston. This reserved, shy English aristocrat is said to have found it difficult to talk to women. In fact, he

[79] Rutherford's university thesis is entitled "*Dissertatio Inauguralis de aero fixo dicto, aut mephitico*" (Inaugural Dissertation on Fixed or Mephitic Air).

[80] See West, J.B., *American Journal of Physiology Lung Cellular and Molecular Physiology, 307*, L1-L6, 2014.

used a private staircase in his London home to avoid any encounter with one of his "female servants". Always well dressed, even if his suits were a bit dated, this taciturn scientist was an extravagant loner. This unique character, who refused to participate in conversations with more than two people, was motivated by personal curiosity, which is why he delayed publishing the results of his research. In fact, many of his results were brought to light by James Clerk Maxwell, who discovered them in the papers Cavendish left behind after his death. It is said that when Cavendish was dying in February 1810, he asked his "servants" to leave him alone and to leave the room where they were gathered. He was found dead a short time later. Thanks to the various legacies he was able to obtain, the English chemist was able to amass a considerable fortune, prompting the French mathematician Jean-Baptiste Biot (1774-1862) to say that he was "the richest of all the scholars, and probably also the most learned of all the rich".

Born in Nice, France, Cavendish began his studies at London's Hackney Academy, a private institution run by opponents of the Church of England (the *Dissenters*), before entering Peterhouse College at Cambridge University in 1748, which he left in 1751 without graduating, perhaps because of religious opposition. Supported by his politically active father, Lord Charles Cavendish, he moved to London, where he established his own laboratory. He was elected a Fellow of the Royal Society at the age of 29 and attended its meetings regularly. He became interested in what he called *factitious air*, i.e. "any kind of air which is contained in other bodies in an inelastic state, and is produced from thence by art". He studied the chemical action of acids on metals, noting in 1766 that the reactions[81] between saltpeter (hydrochloric acid) and zinc, or between vitriol oil (sulfuric acid) and iron, produced *flammable air*. Cavendish thus demonstrated the existence of an explosive gas, not very abundant in the air, which we now call hydrogen (H_2). In an experiment conducted in 1781, he also observed that water was formed when this combustible air was burned in the presence of *dephlogisticated air* (oxygen O_2). Some of his colleagues mistakenly claimed that the *flammable air* he had just isolated was, in fact, the phlogiston that had been sought for centuries. Cavendish informed Priestley of his discovery but was slow to publish his results so Scottish engineer James Watt's 1783 paper on the composition of water preceded Cavendish's, leading to a controversy over the priority of the discovery.

Also in 1766, Cavendish studied the properties of fixed air (CO_2), previously produced by Joseph Black, and showed that this "air" was 1.57 times heavier than ordinary air. He produced this CO_2 by a reaction between acids and alkalis and collected the gas in an inverted flask above a volume of water or mercury included in a container. This is the principle of the eudiometer. In 1777, Cavendish discovered that the air released by animal respiration consisted of *fixed air* (carbon dioxide) and not, as Priestley had suggested, of *phlogisticated air* (nitrogen).

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[81] The metal-acid reactions involved here are as follows: Zn (*solid*) + 2 HCl (*liquid*) → $ZnCl_2$ (*aqueous*) + H_2 (*gaseous*) and Fe (*solid*) + H_2SO_4 (*aqueous*) → $Fe(SO_4)$ (*liquid*) + H_2 (*gaseous*). Both produce hydrogen H_2 in the gaseous state. The phase of the products involved is indicated in brackets.

Beginning in 1781, Cavendish attempted to determine the proportions of various gases in the atmosphere. Again, the chemist used his eudiometer to determine the concentration of dephlogisticated air (oxygen)[82]. Nitrous oxide (N_2O) was injected into a chamber containing a volume of ordinary air and partially filled with water. The reaction of this "laughing gas" with dephlogisticated air (oxygen) produced nitrogen dioxide (NO_2). This gas, which is soluble in water, gradually dissolved in the liquid in the enclosure; by measuring the reduction in the volume of air trapped in the enclosure, the oxygen content could be determined. Cavendish showed that ordinary air is one-fifth dephlogisticated air (oxygen) and four-fifths phlogisticated air[83] (nitrogen).

On the basis of similar experiments carried out on numerous occasions in and around London, he concluded that the composition of air is invariable, even when weather conditions are disturbed. His experiments allowed him, for the first time, to quantify the proportions of the two main gases that make up the air: 79.16% phlogisticated air and 20.84% dephlogisticated air (after excluding CO_2 from the gas mixture and ignoring the possible presence of very minor species). These values are close to the proportions observed today. However, Cavendish showed that a small residue of air, representing 1/120 of the volume of the phlogisticated air, remained unidentified. What is this small residue? We had to wait more than a century for the answer, which came in 1895 from John William Strutt (Lord Rayleigh) (1842-1919) and Sir William Ramsay (1852-1916).

For most of his career, Cavendish used the language characteristic of the phlogiston theory. However, when the latter was fundamentally challenged by Lavoisier, as we shall see in the following pages, the English chemist was probably the first scientist outside France to convert to the new doctrine. As Ramsay writes in his book on atmospheric gases, of all the pneumatic chemists of the time, Cavendish is undoubtedly the most peculiar character, but he is undeniably an extraordinary genius.



FIGURE 3.6: Left: Daniel Rutherford. Right: Henry Cavendish.

[82] Cavendish, H., An account of a new eudiometer. *Philosophical Transactions of the Royal Society of London 73*, 106-135, 1783.

[83] In modern terms, according to Cavendish, air contains four times more nitrogen than oxygen.

Proponents of the Oxygen Theory

Mayow. The second hypothesis is known as the *oxygen* or *pneumatic theory.* To understand the gradual development of this theory, we must first examine the work of the Scottish chemist and physician Johannes (John) Mayow (1641-1679). Mayow, a younger contemporary of Robert Boyle, was a brilliant man. Born in the parish of St. Dunstan in London, he was admitted to Oxford University at the age of 16, where he earned a degree in law and then a diploma in medicine. With little interest in legal matters, he established himself as a practicing physician in the small town of Bath. Mayow was aware of Boyle's work, showing that air was an indispensable ingredient in combustion. In 1668, he pointed out that air can be divided into two distinct components: one called *active air* and the other *inactive air*. And it's only the active component of air, which he called *spiritus igneo aereus*, that contributes to combustion[84].

Mayow also pointed out that combustion and respiration are very similar processes. To confirm this, he repeated Rutherford's experiment and found that the mouse in the upside-down glass suffocated and died after a certain time. This time was reduced by a factor of two when the mouse and the lighted candle coexisted in the same glass. Mayow concluded that the active component of air is essential to life, and that it is probably the lungs that separate active from inactive air. Mayow also believed that *spiritus igneo aereus* is essential for muscle movement, especially of the heart.

Scheele was another figure who played a significant role in the advancement of science at the time, particularly in the development of the oxygen theory. Carl Wilhelm Scheele was born in 1742 in Stralsund, a small town on the Baltic Sea in the Duchy of Pomerania, opposite the island of Rügen. He was the seventh of eleven children in a poor family; his father was a carpenter. At the time, the city, now German, was part of the Swedish dominion within the Holy Roman Empire. Scheele's interest in chemistry began at an early age, and he was introduced to the fledgling discipline through a book[85] by Caspar Neumann (1683-1737). From the age of 14, Scheele devoted himself to pharmacy, first working as an apprentice in the pharmacy of Martin Anders Baulch in Gothenburg before being hired by the Kjellström pharmacy in Malmö. He became a professor at Uppsala University in 1770 and was elected to the Royal Swedish Academy of Sciences in 1775. He lived for several years in the small Swedish town of Köping, west of Stockholm, where he took over the pharmacy left vacant by the death of its owner. His work as a pharmacist and then as a university professor gave him the opportunity to prepare medicines by mixing different substances, to study numerous chemical reactions, and to discover several molecules. In particular, he identified manganese and tungsten, citric and lactic acids, cyanide (1782), fluoride (1771), and hydrogen sulfide. In 1774, he also produced "dephlogisticated muriatic acid". This is chlorine gas (Cl_2) produced by a reaction between muriatic acid (hydrochloric

[84] See the treatise by John Mayow entitled *Tractatus Quinque Medico-Physici*, Oxford, 1674.

[85] Neuman, C., *Les Praelectiones chymicae,* Berlin, 1740.

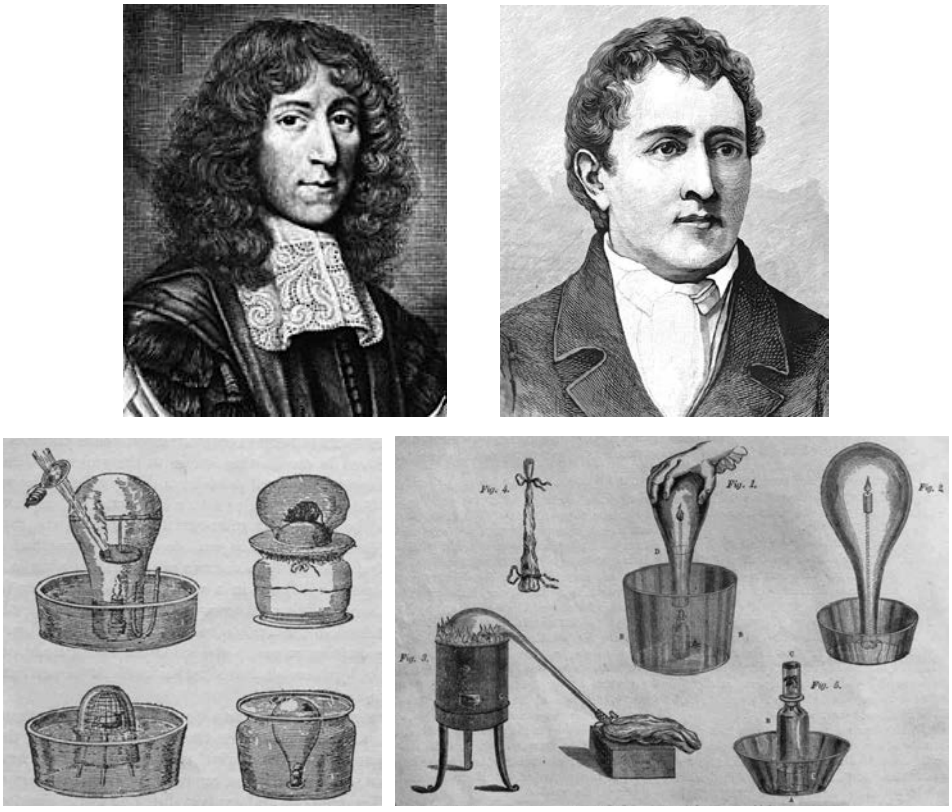


FIGURE 3.7: Top: Left: John Mayow. Right: Carl Scheele. Bottom: Left: Mayow's experiment on the combustion and respiration of a mouse. Source: Partington JR. *Everyday Chemistry. London:* Macmillan; *1938.* Right: Instruments used by Scheele and depicted in his treatise "*Chemical Observations and Experiments of Air and Fire*". Source: Brown R, editor. *Science for all, pictorial marvels &* wonders in Nature vol. 2. London, Cassell & Company, c. *1880.*

acid, HCl) and manganese dioxide, MnO_2[86]. Scheel also discovered that air contains ammonia by simple deduction: he noticed that a thin film of ammonium chloride had formed on the top of a bottle of hydrochloric acid.

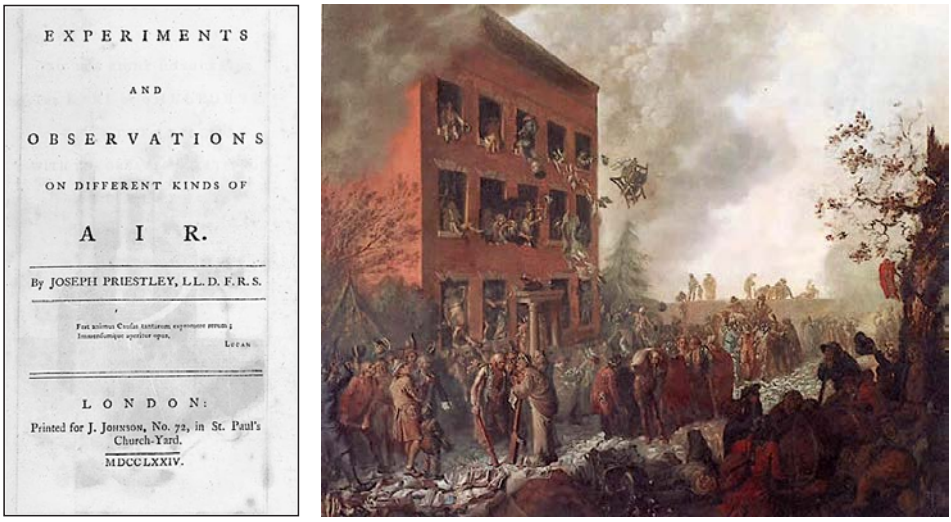
Scheele is remembered as a modest and humble man, but also as a talented experimenter. He was well acquainted with the theory of phlogiston, authoritatively stated by Stahl in the early eighteenth century. He was particularly interested in the role of air in chemical processes. At that time, the air was considered a neutral element: chemical reactions took place without any interference. However, at the suggestion of a renowned professor at Uppsala University, Torbern Olof Bergman (1735-1784)[87] Scheele studied the chemical properties

[86] Also known at the time as "salt spirit".

[87] Member of the Swedish Academy of Sciences, Fellow of the Royal Society in London and foreign member of the Académie des Sciences in Paris.

of various metal oxides, especially manganese and mercury. As early as 1771, he concluded from his studies that air is a mixture of two compounds: on the one hand, *"fire air"* (*Fuerluft*, corresponding to oxygen), which enables combustion, and on the other hand, *"foul air"* (*verdorbene Luft* corresponding to nitrogen), which is inert[88]. He noted that "fire air" is slightly heavier than ordinary air, and "foul air" is slightly lighter. Scheele thus discovered oxygen before Priestley, but his interpretation was based on the phlogiston theory. In his treatise *"Chemische Abhandlung von der Luft und dem Feuer"*[89] written in 1775 but not published until 1777 (two years after Priestley, to whom the discovery of oxygen is attributed), Scheele indicated:

> "Air is made up of two fluids, different from each other, one of which has no ability to attract phlogiston, while the other, which represents between the third and fourth parts of the total mass of air, is particularly suited to such attraction."


EXPERIMENTS

AND

OBSERVATIONS

ON DIFFERENT KINDS OF

A I R.

By JOSEPH PRIESTLEY, LL. D. F. R. S.

Fert animus Cæsar tantarum exempla rerum;
Immanesque ausus aperire opus.

LUCAN

LONDON:

Printed for J. JOHNSON, No. 72, in St. Paul's Church-Yard.

MDCCLXXIV.

FIGURE 3.8: Left: The cover of Priestley's book Experiments and observations of different kinds of air. Right: Priestley's Birmingham home looted and burned by an angry mob on July 14, 1791.

Scheele's conclusions about *"fire air"* challenged the phlogiston theory, which had been criticized by certain chemists who had observed in their laboratories that certain metals subjected to combustion gained weight instead of losing it. According to Scheele's theory, the mass of phlogiston contained in these metals and responsible for the combustion should therefore be negative... which is obviously not possible. Despite his intuition, Scheele never fully challenged the

[88] The expression *fire air* is translated as *air de feu* in French and *Feuerluft* in German. Similarly *foul air* is translated as *air vicié* in French and *verdorbene Luft* in German.

[89] Scheele, C.W., *Chemical treatise on air and fire,* Upsala and Leipzig, 1777.

phlogiston hypothesis, no doubt because it remained too firmly rooted in people's minds and was supported by all the scientists of the time. He did, however, write about the hypothesis:

> "Since phlogiston is a substance, which always presupposes the existence of weight, I have great doubts that such an assumption is well-founded."

This was challenged by Antoine Lavoisier, to whom Scheele shared the results of his work. Exposed to dangerous substances such as arsenic and mercury, which he often used in his laboratory experiments, Scheele died prematurely in 1786 at the age of 43, probably as a result of mercury poisoning. Seeing his death coming, and probably to leave his meager fortune to the woman who had offered him a pharmacy, Scheele married Sara Margaretha Pohl, the widow of the Köping pharmacist, two days before his death.

The debate between proponents of the phlogiston theory and the oxygen theory continued, with Johann Heinrich Pott in Berlin arguing that the phlogiston concept should be considered a "fire principle" rather than a specific chemical substance. Other chemists, such as Giovanni Antonio Giobert (1761-1834) in Italy, rejected Stahl's theory altogether. His paper, submitted in 1792 to the Royal Academy of Turin, was entitled: *"Examen chimique de la doctrine du phlogistique et de la doctrine des pneumatistes par rapport à la nature de l'eau"* (Chemical examination of the doctrine of phlogiston and the doctrine of pneumatists in relation to the nature of water).

Priestley. The work of Joseph Priestley (1733-1804) in England brought science a step closer to the theory of oxygen, although this famous chemist was a proponent of the phlogiston theory. Priestley was an inquisitive and controversial man. Born on March 24, 1733, in Birstall, Yorkshire, 10 kilometers from Leeds, he grew up in a family that belonged to the English *Dissenters*, a group at odds with the official Church of England. This group opposed government control of religious affairs and advocated freedom of thought. In the early 1750s, Priestley received his religious training at an academy founded by the Obedience, which enabled him to become a priest and serve in several churches and parishes founded by the Dissenters. Dissenters were not allowed to enroll at Cambridge or Oxford universities, serve in the army, or stand for election to Parliament.

Interested in the progress of science, Priestley rejected religious dogmatism and mysticism in favor of rationalism and determinism. For him, religious doctrine was acceptable only if it corresponded to what nature taught. He was to become a leading educator, always eager to defend his view of religion and science. In 1761, he published a grammar of the English language that is considered a masterpiece[90]; this work marked the first real break with the concepts of Latin grammar. During his studies, Priestley familiarized himself with Latin, Greek, and Hebrew. He also studied French, German, Italian, and Arabic.

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[90] Priestley, J., *The Rudiments of English Grammar adapted to the use of the schools with observations in style,* Printed for R. Griffiths, 1761.

Although not trained as a physicist or chemist, Priestley was interested in the development of scientific knowledge and its relationship to the Christian religion. In 1767, for example, he wrote a magnificent work on the history of electricity[91]. But he increasingly turned his attention to questions of political philosophy, adopting liberal positions that were sometimes quite radical. For example, he openly railed against the British government, which he believed was severely restricting individual liberties. He also called for greater freedom of thought for believers, which led him to support the founding of the first Unitarian congregation in 1774, based at Essex Chapel in London.

From 1772, Priestley, now in Calne, Wiltshire, conducted experiments to determine the chemical composition of air. He wanted to understand the role of phlogiston in the combustion process. His experiments led him to identify several gases that make up air: *salty air* (i.e., hydrochloric acid HCl), *nitrous air* (nitric oxide, NO), *alkaline air* (ammonia NH_3), *vitriolic air* (sulfur dioxide SO_2), *dephlogisticated nitrous air* (nitrous oxide N_2O), and several others. Nitrous air (NO) was produced by the action of *strong water* (nitric acid) on copper. Priestley noticed that this gas took on a reddish hue when exposed to air. He was observing the formation of the gas we now call nitrogen dioxide (NO_2).

In 1772, Priestley noted that burning coal consumed one-fifth of *ordinary air* produced *fixed air* (carbon dioxide, CO_2), but did not interact with an apparently inert gas he later called *phlogisticated air* (nitrogen, N_2). In August 1774, he announced that he had been able to isolate "a new kind of air" which he called *dephlogisticated air* (oxygen O_2); this appeared after he had focused (with a lens) solar rays to heat red oxide of mercury in a sealed container[92]. Priestley brought back this *calcined mercury* from his visit to Lavoisier in Paris. He found that this gas allowed combustion and respiration to occur more efficiently than with *ordinary air*. In fact, he found that a mouse in a hermetically sealed enclosure lived twice as long when ordinary air was replaced by dephlogisticated air. Priestley, who was probably aware of Scheele's work in Sweden and especially of his discovery of *fire air* around 1771, published his results in 1774, three years before Scheele's late publication. His work was submitted to the Royal Society in 1775 and appeared in 1776 in a volume entitled *Experiments and Observations on Air*.

Despite his discovery of oxygen, Priestley never questioned the phlogiston theory. On the contrary, he defended it throughout his life, using it, for example, to show the relationship between *dephlogisticated* air, respiration, and blood. He considered *dephlogisticated* air to be ordinary air from which some of its phlogiston had been removed. He added that *dephlogisticated air* combined with phlogiston would sustain combustion longer than with ordinary air. His attitude, however, isolated him from his younger colleagues who formed the group of "new chemists" influenced by Lavoisier's work.

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[91] Priestley, J., *The History and Present State of Electricity, with Original Experiments*, Printed for J. Dodsley, J. Johnson and T. Cadwell, London, 1767.

[92] Metal oxides are called "calx" from the Greek χάλιξ (*khaliks*, "pebble"). The phlogiston theory considers them to be elemental substances produced by a combustion process and therefore devoid of phlogiston.

In the late 1780s, Priestley further emphasized his political radicalism, supporting, for example, the American (1765-1783) and French (1789-1799) revolutions. In 1791, he and some of his English religious dissident friends attended a banquet in his hometown of Birmingham to celebrate the storming of the Bastille in Paris on July 14, 1789. Political opponents burst into the room and directly attacked the guests. Some were injured. The riots continued for three days: several houses and churches were destroyed by fire; Priestley's house and laboratory were burned down. The Académie des Sciences de Paris, through its *secrétaire perpétuel,* the Marquis Nicolas de Condorcet[93] (1743-1794), thanked the English scientist for his sympathy for France. In Paris, the government granted Priestley the title of French citizen and even parliamentary representative of Orne, which he refused. In 1793, Priestley and his wife, Mary Wilkinson, decided to emigrate to the United States because of the continuing political situation in England. The family settled in Northumberland, Pennsylvania, where Priestley founded the first Unitarian church. He died on February 6, 1804, at the age of 70. But that did not stop the Birmingham City Council from erecting a statue in 1874 to honor the man who had been persecuted by his fellow citizens a century earlier.

Box 3.1. Eudiometry[94]

In the eighteenth century, the question of public health preoccupied a large number of chemists who wanted to be able to measure the purity of the air, which in turn was determined by the amount of *vital air*, i.e. the oxygen contained in *ordinary air.* The absence of *vital air* is easily determined by suffocating a mouse or bird in a hermetically sealed enclosure and exposing it to the gas mixture being analyzed. However, the use of small animals for such experiments posed serious problems. First, these animals suffered before they died, and second, the management of these small animals in pneumatic chemistry laboratories required a great deal of attention. This led Stephen Hales, who had been experimenting on the relationship between the nature of "air" and respiration using the pneumatic tank he had invented, to ask the French engineer and mathematician Alexandre-Julien Savérin[95] (1720-1805) to build a more compact instrument capable of determining the purity of gas mixtures without endangering the lives of mice or other animals. Savérin's *queynometer*, which measured the compressibility of air, was designed to meet this need. At the time, it was known that impure air was impregnated with harmful particles and lost its elasticity. From this point of view, measuring the compressibility of air provided information on its purity. However, Savérin's queynometer was hardly ever used.

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93 Marie Jean Antoine Nicolas de Caritat, Marquis de Condorcet.

94 See in particular Pere Grapí's *Inspiring Air, A history of air-related science*, Vernon Press, 2019.

95 Author of "Histoire critique du calcul des infiniment - petits", containing "La métaphysique" and "la théorie du calcul" (1753) and "L'histoire des philosophies modernes" (1760-1767).

Another, more promising instrument, the *eudiometer*[96] was designed in 1775 by the Italian physicist, chemist, and meteorologist Marsilio Landriani (1751-1815) to determine the purity of the air. Its shape was that of a graduated cylindrical glass tube, reminiscent of the mercury thermometer or barometer. The principle used was similar to that of the pneumatic tank, but this time the device was portable and could, in principle, determine the purity of the air in different locations, thus helping to improve the health of certain areas in polluted cities.

When the eudiometer was introduced into the laboratories of the "pneumatic chemists", the phlogiston theory was still in vogue, and the instrument was initially intended to indirectly determine the effect on the air of this substance emitted during combustion, which no one had yet been able to measure; phlogiston was then considered an immaterial principle that could not be directly detected. With the growing conviction that air is composed of different gases and that only one of its components is breathable, eudiometers were then used to determine the proportions of different chemical substances present in a gaseous mixture. In 1785, Henry Cavendish used such an instrument to determine the amount of oxygen in the air. A few years earlier, the Dutch biologist Jan Ingenhousz (1730-1799) had used an eudiometer to show that plant leaves emit oxygen when exposed to light, demonstrating the process of photosynthesis.

The principle on which the eudiometer is based was established by Joseph Priestley in 1772. The British scientist studied the reaction between *nitrous air* (i.e., nitrogen oxide NO) and *vital air* (i.e., oxygen O_2). The nitrogen dioxide resulting from this reaction appeared in a volume located in the upper part of the glass tube above the water column of the instrument. Because nitrogen dioxide is soluble in water, the volume of gas at the top of the tube tended to shrink as the gas mixture became more oxygenated. The graduation on the instrument's glass tube showed how the water column rose in the tube, allowing to deduce the concentration of *vital air*.

In 1777, Count Alessandro Volta (1745-1827), a friend of Landriani, used a special eudiometer to determine the flammability of the gases he was studying. To do this, he inserted two electrodes into the device's sealed casing, creating a spark inside the volume containing the gas mixture to be analyzed. If the spark was followed by an explosion and the plug was ejected, the air was declared flammable.



FIGURE 3.9: Landriani's eudiometer invented in 1775. Source: Chemistry World.

[96] Word composed of the Greek words εὔδιος (eudios), meaning serenity, calm, and μετρον (metron) meaning measure.

Volta had just invented a new type of pistol that eliminated the need for traditional gunpowder. He used this device to study the properties of *swamp gases* that he had collected near Lake Como in Italy, allowing him to detect the presence of methane in the atmosphere for the first time.

The eudiometer played an important role for many centuries for the followers of pneumatic chemistry and became a central part of laboratories dealing with air chemistry.

Lavoisier. In Paris, Antoine-Laurent de Lavoisier also worked on the problem of combustion and respiration. Today, this brilliant mind is considered the inspiration behind the *chemical revolution* that took place at the end of the 18th century, just as another revolution was getting underway: the French Revolution.

Lavoisier was born into a noble family. He began his literary education at the Collège Mazarin in Paris before studying law. He received his bachelor's degree in 1764 and was admitted to the Paris bar, but never practiced law. His father frequently organized meetings with the most fashionable scientists of the day, allowing the young Antoine-Laurent to rub shoulders with mathematicians, astronomers, and physicians and to develop an interest in the sciences. Abbé Nicolas-Louis La Caille recommended meteorology to Lavoisier, and Abbé Jean-Antoine Nollet introduced him to experimental science. These two ecclesiastics exerted a considerable influence on the young lawyer, who thus discovered the secrets of chemistry.

However, Lavoisier initially turned to administrative and financial functions. In 1768, he became a member of the *Ferme Générale*, an institution of the ancien regime responsible for collecting taxes on behalf of the king. The Ferme was also responsible for the production of gunpowder and had a monopoly on the production and sale of tobacco in France. The economic interests of the Ferme were gigantic, allowing its owners to receive dividends on the profits made and the Fermiers Généraux to enrich themselves considerably. This made them very unpopular with the public. In 1771, at the age of 28, Lavoisier married the 13-year-old daughter of another Fermier Général, Marie-Anne Paulze (1758-1836). In the years that followed, this charming and brilliant woman contributed directly to the research work begun by her husband (see Box 3.3).

Lavoisier, who became a member of the Académie des Sciences de Paris in 1769 after two unsuccessful attempts, devoted much of his time to his research into chemical processes. His considerable financial resources enabled him to equip his laboratory, which served as a model for chemists of the time.

In 1772, Lavoisier conducted a study on the *release or fixation* of an *elastic fluid* resulting from the combustion process. This work marked the beginning of the chemical revolution, which was closely linked to the career of this illustrious scientist (Box 3.2). On November 1 of that year, he went to the Académie to hand the secretary a sealed envelope announcing an important discovery:

> "I discovered that sulfur, far from losing its weight when burned, actually gained weight. [...] The same is true of phosphorus. This increase in weight is due to a prodigious quantity of air that fixes itself during combustion and combines with the vapors."

He went on to explain the reasons for his decision[97]:

"As this discovery seems to me to be one of the most interesting that has been made since Stahl, I thought it my duty to secure ownership of it, by making the present deposit at the Academy, to remain secret until such time as I publish my experiments".

Lavoisier's envelope was opened at a session of the Académie on May 5, 1774.

By demonstrating that the calcination of sulfur and phosphorus fixes a quantity of air, with a consequent increase in weight, Lavoisier fundamentally challenged Georg Ernst Stahl's theory that metals lose their phlogiston during calcination. He then extended his study to the combustion of other materials such as tin. In 1774, he submitted to the Académie a report on the calcination of this metal, which read as follows

"In any calcination of tin, the increase in weight of the metal is exactly equal to the weight of the quantity of air absorbed, which proves that the portion of air which combines with the metal [...] is about equal in specific gravity to the air in the atmosphere."

A year later, the military apothecary Pierre Bayen (1725-1798), chief pharmacist of the king's armies, pointed out that a century and a half earlier, the Perigordian physician Jean Rey (1583-1645), whose work was quickly forgotten, had reached similar conclusions. Lavoisier did not react immediately, but in his posthumous memoirs, published by his wife in 1805, there is an explicit reference to Rey's earlier work[98]:

"One of the earliest writers on this subject is an almost unknown physician named Jean Rey, who lived at Bugue in Périgord at the beginning of the 17th century, and who was in correspondence with the small number of people who cultivated the sciences at that time. Descartes and Pascal had not yet appeared; neither Boyle's nor Torricelli's vacuum was known, nor was the cause of the ascent of liquors in tubes empty of air. Experimental physics did not exist; chemistry was in the dark. However, Jean Rey, in a work published in 1630 on the investigation of the cause for which lead and tin increase in weight when oxidized, developed such profound views, so analogous to the doctrine of saturation and affinities, that I have long been unable to escape the suspicion that Jean Rey's Essays were composed at a much later date than that shown on the work's frontispiece."

However, according to a note preserved in the British Museum, Lavoisier repurchased all circulating copies of the "Essays" published by Jean Rey in 1630, no doubt to preserve the primacy of his discovery.

In the fall of 1774, the Lavoisiers invited Joseph Priestley to dine with them when he accompanied a high-ranking English dignitary to Paris. The British chemist took the opportunity to discuss the mysterious air he had produced by calcining mercury red and lead red. Lavoisier was intrigued by these results and after dinner, invited

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[97] Lavoisier A.L., Œuvres publiées par les soins du Ministre de l'Instruction publique, sous la direction de Dumas et Grimaux, Tome II, Imprimerie nationale, Paris, 1864-1893.

[98] Lavoisier, A.-L. de, *Mémoire de Chimie*, Vol. II, 79-80, Paris, 1805.

Priestley to repeat his experiment in the attic laboratory set up in his Paris home in the Arsenal near the Bastille. The French chemist decided to investigate the matter further. In early 1775, he performed several experiments. First, he mixed the calx of mercury (HgO) with powdered charcoal and observed the outgassing that occurred: it was indeed the *fixed air* (CO_2) already identified by Black[99]. He then repeated the experiment, but this time without adding coal. The gas produced by strongly heating the calx of mercury was of a different nature, because it supported respiration and combustion[100]. Lavoisier first called "vital air" the "eminently breathable part of air" and "mofette gas" the gas that does not contribute to respiration. He openly attacked the phlogiston theory, asserting that combustion is not the dissipation into the air of a mysterious phlogiston initially contained in the fuel. On the contrary, combustion is characterized by the absorption of an air component by the fuel. And on September 5, 1777, in a paper submitted to the Académie, he wrote:

> "I shall henceforth designate dephlogisticated air or eminently breathable air [...] by the name of the acidifying principle or oxygen principle."

In this way, the word "oxygen" was created to denote an elementary substance capable of producing acids, whose epidemiological origins lie in the Greek words *οξυς* (oxus, acid) and *γενος* (genos, which creates). The concept of phlogiston, and thus Stahl's chemistry, disappeared in favor of the oxygen theory and modern chemistry, on which even today's work is based.

One of Lavoisier's fundamental contributions was the realization that the mass of the elements is conserved in any chemical process. In a nutshell, this discovery made chemistry a quantitative science: nothing is created, nothing is lost, everything is transformed. Lavoisier wrote in his *Traité élémentaire de Chimie*:

> "Nothing is created, neither in the operations of art, nor in those of nature, and we can posit in principle that, in any operation, there is an equal quantity of matter before and after the operation; that the quality and quantity of the principles is the same, and that there are only changes, modifications."



FIGURE 3.10: Left: Portrait of Joseph Priestley by Ellen Sharples in 1794. Right: Antoine Laurent de Lavoisier and his wife Marie-Anne Pierrette Paulze, painted by Jacques-Louis David in 1788.

[99] This is the reaction between mercury oxide and carbon: $2\ HgO + C \rightarrow 2\ Hg + CO_2$ where carbon dioxide is Black's fixed air.

[100] In this case, the reaction is $2\ HgO$ (solid) $\rightarrow 2\ Hg$ (liquid) $+ O_2$ (gas) where the oxygen molecule represents Lavoisier's eminently breathable air.

The *mofette gas* that doesn't contribute to combustion was called *azote* by Lavoisier, a name composed of an *a-privative* and the Greek radical ζωτ (*dzôê* or, in French, "vivant"), meaning "deprived of life". The chemical symbol is *N*, from the Latin word *nitrogenium*.

Box 3.2. Lavoisier's Famous Air Analysis Experiment.
Text taken from A. Berget, *Les problèmes de l'Atmosphère*, Flammarion, 1914 and modified.

In 1777, Lavoisier performed a famous experiment in which he determined both the complexity of air and its composition. He took a balloon containing mercury, the neck of which, bent twice, was placed under a bell filled with air and resting on a vat of mercury; the mercury in the balloon was heated to boiling point, while that in the vat on which the bell rested was cold. After carefully recording the temperature, pressure and volume of the air trapped under the bell, the mercury in the balloon was brought to the boil and kept there for twelve full days. At the end of this time, it was found that the mercury in the balloon was covered with a red powder; this was mercury oxide, formed by the direct union of the metal with the oxygen confined in the apparatus. After the entire apparatus had cooled, the volume of gas remaining was only about 6/7 of the original volume; it consisted of a gas completely unsuitable for breathing. To complete his demonstration, Lavoisier collected the red films formed on the mercury, heated them in a small glass matrass and carefully collected the resulting gas. The volume of this gas was exactly equal to the decrease in volume observed in the previous experiment; the gas collected in this way strongly supported combustion: it was *oxygen*. On the other hand, the residual gas from the first operation sustained neither combustion nor life; animals introduced under a bell jar filled with it succumbed to asphyxiation: this was *nitrogen*.

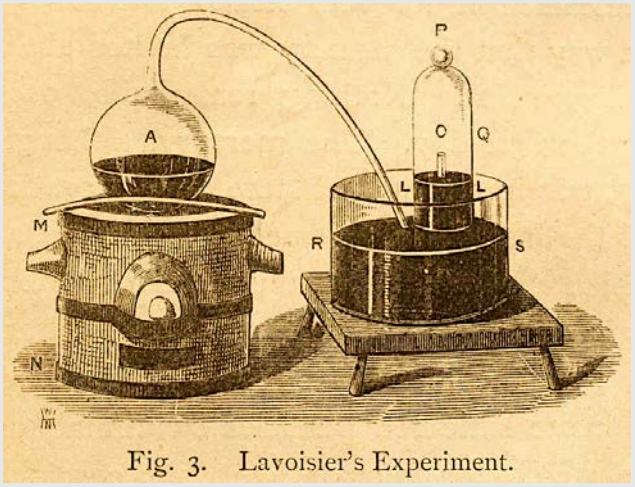


FIGURE 3.11: Lavoisier's experiment to analyze the chemical composition of air. Source: Hartley W.N., Air and its relations to life, Longmans Green & Co, 1876.

Box 3.3. Marie-Anne Pierrette Paulze-Lavoisier (1758-1836)[101]

Marie-Anne Paulze, born on January 20, 1758, in Montbrison, Loire, was an interesting and engaging personality who made a major contribution to the work of Antoine-Laurent Lavoisier, whom she married on December 16, 1771. Daughter of the Fermier Général Jacques Paulze, she was introduced to chemistry by the chemist Jean-Baptiste Bucquet (1746-1780), who collaborated with her husband. She also studied English, Italian, and Spanish. She took Latin lessons from her brother Balthazar and read ancient Greek. Her knowledge enabled her to translate the publications of several foreign scientists, including the British chemists Joseph Priestley and Henry Cavendish, and the Irish geologist Richard Kirwan[102] (1733-1812), one of the last proponents of the phlogiston theory. She also took up drawing under the guidance of the painter Jacques-Louis David[103] (1748-1825), which enabled her to produce a number of illustrations that appeared in books published by her husband, notably the *Traité Élémentaire de Chimie*. The Lavoisiers, who initially lived on the rue Neuve-des-Bons-Enfants in Paris, moved in 1776 to the Arsenal, near the Bastille, in the luxurious Hôtel des Régisseurs, which was made available to Lavoisier as head of the Régie des poudres et salpêtres.

Intelligent, refined and seductive, Marie-Anne Paulze, who was both a woman of the world and a woman of character, organized social evenings and meetings at the Arsenal, attended by the best minds. These included the American ambassador to the Court of Versailles, Benjamin Franklin; the engineer James Watt; the mathematicians Joseph-Louis Lagrange and Gaspard Monge; the chemists Claude Berthollet, Joseph Priestley and Henry Cavendish; the physicist Pierre Simon de Laplace; the astronomer and future mayor of Paris, Jean-Sylvain Bailey; and the economist and entrepreneur Pierre-Samuel Dupont de Nemours (1739-1817). It was with the latter that Marie-Anne Paulze began her love affair in 1781. In 1799, Pierre-Samuel Dupont de Nemours emigrated to the United States, where his son Éleuthère, a former student of Lavoisier, opened a gunpowder factory that would become the foundation of the famous *Dupont de Nemours* company, one of the largest industrial groups in the world today. On leaving Europe, Dupont de Nemours wrote a letter to Marie-Anne Paulze that revealed the complex nature of their relationship:

> "You have to love yourself, with one nuance or the other. It's my experience that you're not suited to friendship. You have neither its outpourings, nor its interest, nor its consolations, nor its advice, nor its caresses,

[101] See also: Jacques, Éric, *Lavoisier*, Ellipses, 420 pp., 2019 and Viel, Claude, Le salon et le laboratoire de Lavoisier à l'Arsenal, cénacle où s'élabora la nouvelle chimie, *Revue d'histoire de la pharmacie*, 306, 255-266, 1995 and Peumery, Jean-Jacques, Marie-Anne Pierrette Paulze, épouse et collaboratrice de Lavoisier, *Vesalius, VI*, 2, 105-113, 2000.

[102] Richard Kirwan's work is entitled "*Essay on Phlogiston and the Constitution of Acids*". In her translation, Marie-Anne Paulze has added footnotes criticizing the work and highlighting errors.

[103] Painter Jacques-Louis David, a supporter of the French Revolution and friend of Maximilien Robespierre, was President of the National Convention in 1794.

nor its speeches, nor its sweet silence. Where your tenderness ends, everything ends. You become cold, hard, quarrelsome, and it's the derogatory expression that lands on your lips all by itself".

Dismissed from his position as head of the powder department by the French Revolution, Lavoisier left the Arsenal in August 1792 and settled on the Boulevard de la Madeleine in Paris. The Arsenal laboratory was dismantled, the manuscripts confiscated, and the instruments turned over to the revolutionary state. After the Fermiers généraux were arrested in November 1793 and sentenced to death by a revolutionary tribunal for embezzling sums that, according to the prosecution, should have gone to the state, Lavoisier was guillotined on May 8, 1794; Marie-Anne was arrested on June 29. The couple's assets, especially their property, were confiscated. But the political situation was changing rapidly, and the incorruptible and bloodthirsty Maximilien de Robespierre (1758-1794), who had launched the Terror, was losing his support in the Assembly of Deputies. On July 27, 1794, he was overthrown and arrested. The next day he was condemned to death without trial and executed that afternoon. Marie-Anne was released on August 17. She then set out to recover her property, in particular the houses on rue Neuve-des-Bons-Enfants and rue de la Madeleine. She wanted to recover her property, in particular the buildings, manuscripts and 13,000 pieces of chemistry equipment and 250 pieces of physics equipment that were part of the laboratory. She retrieved all the manuscripts and equipment shortly before her death.

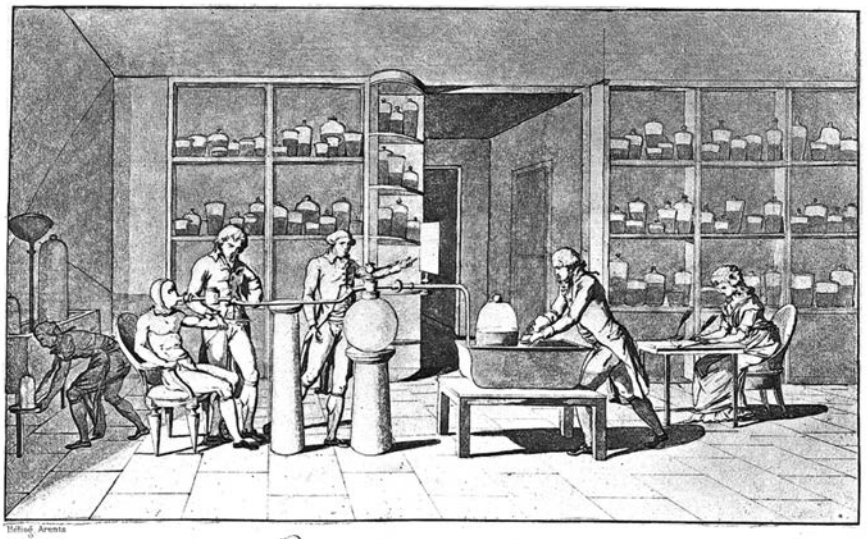


FIGURE 3.12: Respiration experiment in Lavoisier's laboratory in Paris. The seated man performing the experiment is chemist Armand Seguin (1767-1835), who collaborated with Lavoisier. On the right is Marie-Anne Pierrette Paulze, the author of the drawing.

But above all, Marie-Anne Paulze sought to perpetuate the memory of her husband, whom she described as having "such a just mind, such a pure talent, and such a sublime genius". She collected the manuscripts she could recover and published Lavoisier's *Mémoires de Chimie* in two volumes in 1805. In December of the same year, she married the physicist Benjamin Thompson, comte de Rumford (1753-1814), but their relationship, marked by an incompatibility of moods, rapidly deteriorated; the couple divorced in 1809 and the comte de Rumford died in 1814. Marie-Anne Paulze, who remained faithful to her first husband and kept the Lavoisier name, died unexpectedly in Paris on February 10, 1836, at the age of 78.

In addition to his scientific work, Lavoisier pursued other, often more political goals and devoted himself to his work as *Fermier Général*. In 1775, the contract with the Ferme Générale was terminated, and the production of the powder was entrusted to a *régie*, of which Lavoisier became one of the directors. This new position allowed the Lavoisiers to move into the *Hôtel des Régisseurs* in the *Petit Arsenal* near the Bastille. From 1787 to 1790, Lavoisier was a deputy and commissioner for the *Tiers-État* in the *Orléanais Assembly*, and in 1789, he became an elector in the Paris Commune. But with the advent of the Revolution and the storming of the Bastille on July 14, 1789, difficulties mounted. There were rumors that the gunpowder produced under Lavoisier's direction was being sent to the enemies of the country. Considered traitors, Lavoisier and his wife Marie Anne were thrown into prison and eventually released. In 1790, the nobility was abolished, and in 1791, the Ferme Générale was dissolved. Removed from all his posts, Lavoisier felt increasingly threatened. The "Terror" took hold. On August 8, 1793, the Académie and all other learned societies were abolished at the express request of Abbé Henri Grégoire (1750-1831). This priest, who was president of the National Convention for a few days, was one of the bishops elected by a French department rather than appointed by the Pope. The Marquis de Condorcet, permanent secretary of the Académie, was arrested and committed suicide in prison.

On November 24, 1793, Lavoisier and the other Fermiers généraux were also arrested, accused of embezzling money owed to the state (Box 3.4). At the instigation of the parliamentary representative André Dupin de Beaumont (1744-1833), the defendants, considered remnants of the *ancien régime*, were tried and sentenced to death by the Revolutionary Tribunal. During the trial on May 8, 1794, the judge, Jean-Baptiste Coffinhal (1762-1794), denied the defendants the right to speak. To those who tried to save the life of the brilliant chemist, Coffinhal, who was to be guillotined himself a few months later[104] is said to have replied[105]:

> "The Republic has no need of scientists or chemists; the course of justice cannot be suspended."

[104] Coffinhal himself was guillotined on Place de la Grève (today Place de l'Hôtel de Ville in Paris) on "18 Thermidor de l'An II" or August 6, 1794.

[105] See also: Jones, S., *No Need for Geniuses. Revolutionary Science in the Age of the Guillotine*, Abacus (Hachette), 353 pp., 2017.

A few hours after the trial ended, Lavoisier and twenty-seven other fermiers généraux (including Lavoisier's father-in-law, Jacques Paulze) were taken by cart to the Place de la Révolution (now the Place de la Concorde), where they were guillotined. The mathematician Guiseppe Luigi Lagrange (1737-1813), whom Lavoisier had defended when the revolutionaries wanted to expel foreign scientists from France, wrote

> "It only took them a moment to knock this head off, and perhaps a hundred years won't be enough to reproduce a similar one."

Box 3.4. Lavoisier's Arrest

Translated from the book entitled *Lavoisier* by Albert Lévy, second edition, Librairie Hachette, Paris 1882.

Lavoisier's genius was not confined to scientific matters: under Louis XVI, he was one of the first to call for a general reduction of taxes... Appointed a deputy to the Constituent Assembly, he was a member of the commission in charge of the treasury [...]. Finally, Lavoisier was one of the members of the Grand Commission appointed by the Convention to establish a uniform system of weights and measures.

Lavoisier had long since relinquished his position as fermier général when he was arrested on the complaint of a former servant of his father-in-law.

The indictment accused him of being "the author or accomplice of a plot against the French people; of having mixed tobacco with water and ingredients harmful to the health of the citizens who would use it; of having plundered the people and the national property...".

When Lavoisier heard that he was to be arrested, he wandered alone through the streets of Paris, not daring to ask a friend for the dangerous service of a retreat. At last, in the evening, he happened to meet an usher of the Académie des Sciences, the old Lucas, who took him back trembling, and hid him in one of the most secluded corners of the Louvre, where the Académie then held its meetings.

But when Lavoisier learned that his father-in-law and all his colleagues were under arrest, he felt honor bound to share their peril and without hesitation ran to be taken prisoner.

In his dungeon, Lavoisier continued to print his works "with a calm and serenity worthy of ancient times," as Cuvier put it.

On May 6, the accused appeared before the revolutionary tribunal. Lavoisier, forgetting himself, thought only of defending his colleagues. A vain defense! The sentence had already been pronounced. All the defendants were sentenced to death; the execution was to take place within two days!

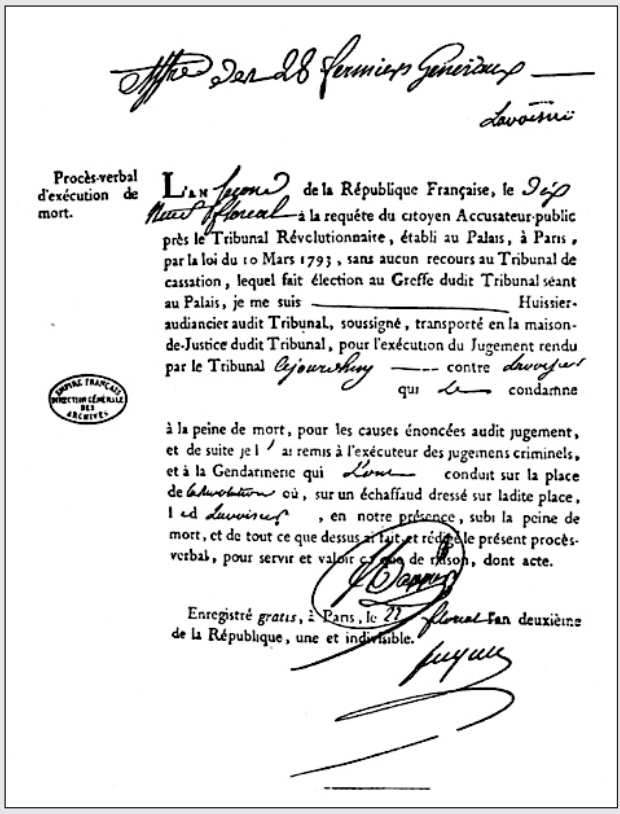
Lavoisier asked for a reprieve, "with a view," he said, "to determining experiments useful to mankind; these were researches on transpiration and animal heat.

"If I'm granted this reprieve," he said, "I'll finish my work, and then I'll gladly sacrifice my life for my country." A reprieve was life! Two months later, Robespierre's death put an end to the Reign of Terror, the revolutionary

laws were abolished, and the prisoners were released. Lavoisier, saved from the scaffold, continued his admirable research and brought new discoveries to science. Unfortunately, he was denied this reprieve.

No one applied for Lavoisier, such was the fear that froze the heart. Where were the members of the Académie, where were Lavoisier's colleagues and collaborators?

On May 8, 1794, the revolutionary axe chopped off the head of France's most famous scientist.



Procès-verbal d'exécution de mort.

L'an … de la République Française, le … … à la requête du citoyen Accusateur-public près le Tribunal Révolutionnaire, établi au Palais, à Paris, par la loi du 10 Mars 1793, sans aucun recours au Tribunal de cassation, lequel fait élection au Greffe dudit Tribunal séant au Palais, je me suis ——— Huissier-audiancier audit Tribunal, soussigné, transporté en la maison-de-Justice dudit Tribunal, pour l'exécution du Jugement rendu par le Tribunal … contre … qui … condamne

à la peine de mort, pour les causes énoncées audit jugement, et de suite je l' ai remis à l'exécuteur des jugemens criminels, et à la Gendarmerie qui … conduit sur la place de … où, sur un échaffaud dressé sur ladite place, l'ed … , en notre présence, subi la peine de mort, et de tout ce que dessus ai fait et rédigé le présent procès-verbal, pour servir et valoir … de raison, dont acte.

Enregistré *gratis*, à Paris, le … an deuxième de la République, une et indivisible.

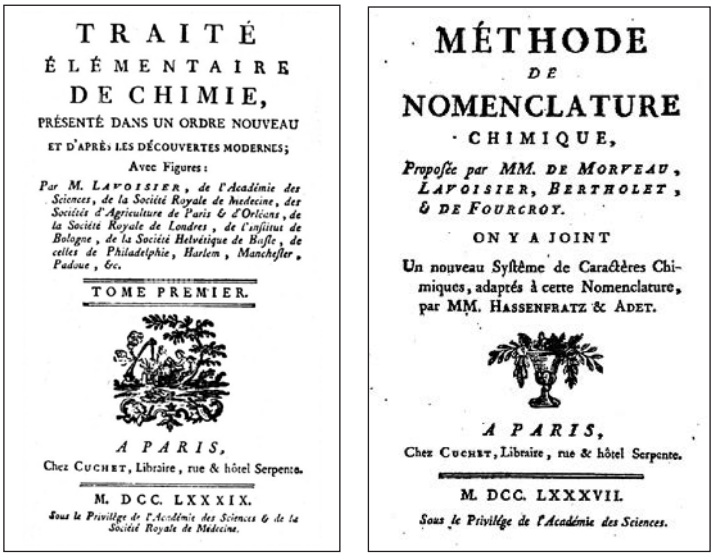
Figure 3.13: Lavoisier's execution report.

Was Lavoisier a genius who brought chemistry into the modern age by demonstrating the importance of physical measurement and introducing mathematical rigor into the analysis of chemical transformations? Or was he simply an intelligent integrator of the work of his colleagues and predecessors? In any case, it was Lavoisier who defined oxygen and its fundamental role in the processes of combustion and respiration. It was also thanks to him and his fellow chemists, Antoine François comte de Fourcroy[106] (1755-1809), Louis-Bernard Guyton,

[106] The son of a poor apothecary, Antoine-François Fourcroy studied medicine and joined the Académie des Sciences in 1787.

Baron de Morveau[107] (1737-1816), and Claude-Louis Berthollet[108] (1748-1822), that the classification inherited from the alchemists was replaced by a methodical nomenclature that anticipated today's system. The four scientists wrote a new *Méthode de nomenclature chimique* that was presented to the Académie royale des Sciences on April 17, 1787. Lavoisier's three colleagues, initially committed to the phlogiston theory, rallied around his views. As for the mathematician Gaspard Monge, Comte de Péluse (1746-1818), known for having developed descriptive geometry and founded the École Polytechnique de Paris, while also being interested in chemistry, he was also an ardent supporter and propagator of Lavoisier's theses.

In 1789, Lavoisier published an elementary treatise that is considered the first modern chemistry textbook[109]. This book establishes a methodology for quantifying the rates at which reactions occur. Influenced by Pierre-Simon de Laplace, Lavoisier introduced a mathematical approach to chemistry. Thanks to his persistence and persuasiveness, the concept of phlogiston, which had dominated thinking for several centuries, was finally abandoned. Stahl's chemistry gave way to the *new chemistry* of Lavoisier.


TRAITÉ
ÉLÉMENTAIRE
DE CHIMIE,
PRÉSENTÉ DANS UN ORDRE NOUVEAU
ET D'APRÈS LES DÉCOUVERTES MODERNES;
Avec Figures:
Par M. LAVOISIER, de l'Académie des Sciences, de la Société Royale de Medecine, des Sociétés d'Agriculture de Paris & d'Orléans, de la Société Royale de Londres, de l'Institut de Bologne, de la Société Helvétique de Bafle, de celles de Philadelphie, Harlem, Manchester, Padoue, &c.
TOME PREMIER.
A PARIS,
Chez CUCHET, Libraire, rue & hôtel Serpente.
M. DCC. LXXXIX.
Sous le Privilège de l'Académie des Sciences & de la Société Royale de Médecine.

MÉTHODE
DE
NOMENCLATURE
CHIMIQUE,
Proposée par MM. DE MORVEAU, LAVOISIER, BERTHOLET, & DE FOURCROY.
ON Y A JOINT
Un nouveau Système de Caractères Chimiques, adaptés à cette Nomenclature, par MM. HASSENFRATZ & ADET.
A PARIS,
Chez CUCHET, Libraire, rue & hôtel Serpente.
M. DCC. LXXXVII.
Sous le Privilège de l'Académie des Sciences.

FIGURE 3.14: Two works that revolutionized chemistry and in which the theses of Lavoisier and his colleagues are set out.

[107] Born in Dijon, Louis-Bernard Guyton de Morveau was a lawyer at the Dijon Parliament. Along with several European colleagues, he advocated a reform of chemical nomenclature.

[108] Born in the Duchy of Savoy, Claude Louis Bertholet studied medicine in Turin and joined the Académie des Sciences in 1780.

[109] Lavoisier, M., *Traité élémentaire de chimie présenté dans un ordre nouveau et d'après les découvertes modernes,* Chez Cuchet, Libraire, Paris, 1789.

However, the conclusions of this work were not immediately accepted by the entire scientific community. The Royal Academy itself was reluctant to endorse the oxygen theory. A commission of scientists charged with examining the ideas of Lavoisier and his three colleagues expressed some skepticism:

> "We therefore believe that this new theory, along with its nomenclature, must be subjected to the test of time, the shock of experience, the sway of opinion that follows; and finally, to the judgment of the public, as the only tribunal from which they must and can emerge. Then it will no longer be a theory, but a chain of truths or an error. In the former case, it will give human knowledge another solid foundation; in the latter, it will be forgotten along with all the theories and systems of physics that preceded it."

In France, many led an offensive against the change in chemical nomenclature to which they had become accustomed. The chemist and politician Christophe Opoix (1745-1840), for example, noted that the words used by previous generations to designate chemical species were widely accepted; they were now being replaced by complicated words that shocked the ear. Chemistry, he wrote[110] in a strange way,

> "was part of good education, and even women assiduously frequented the amphitheaters without finding themselves strangers or out of place."

In Berlin, Lavoisier's findings were also questioned, and his effigy was even burned. In Scotland, Elizabeth Fulhame, a brilliant chemist who had discovered the process of chemical catalysis, rejected both the theories of phlogiston and Lavoisier's views. In her essay on combustion, published in 1794, she spoke of the difficulty for women to work in an almost exclusively male environment:

> "It may seem established to some that I engage in the study of nature, but repugnant to indolence, and having much leisure, my mind has led me to this mode of amusement, which I have found entertaining and will, I hope, be regarded as harmless by the liberal and the learned. But censure is perhaps inevitable; for some are so ignorant that they become sullen and silent, and are frozen with horror at the sight of anything bearing the appearance of knowledge, in whatever form it may appear; and if the *spectre* appears in the shape of a woman, the pains they undergo are mournful indeed."

Additional information about the chemical composition of the atmosphere was obtained in the following years. In 1805, in collaboration with his German friend, the geographer Alexander von Humboldt (1769-1859), Gay-Lussac analyzed in the laboratory air samples taken during hot-air balloon ascents and concluded that the chemical composition of the air varied little with altitude. The two scientists also showed that water consists of two parts hydrogen and one part oxygen. Water vapor (H_2O) is an atmospheric constituent whose content, which is highly variable in time and space, is highest in the lowest layers of the atmosphere.

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[110] See Borvon, G., *Histoire de l'oxygène*, Vuibert, Paris, 215 pp., 2012.

At the end of the Age of Enlightenment, it was known that the dry air in the Earth's atmosphere is composed mainly of nitrogen (N_2, 78%) and oxygen (O_2, 21%), and that combustion and respiration produce carbon dioxide (CO_2). It was also known that hydrogen (H_2) is a flammable gas in small amounts. But the question remained: to which chemical species should the residue observed by Cavendish, representing about one percent of the volume of air, be attributed? The answer was not found until the nineteenth century.

Lomonosov. It's probably worth mentioning that as early as 1756, Mikhail Vasilievich Lomonosov (1711-1765), a Russian scientist little known outside his country, came to the same conclusions as Lavoisier twenty years later. This all-rounder, who was interested in literature, history, and art as well as astronomy, geology, physics, and chemistry, decided to reproduce an experiment carried out by Boyle in 1673, in which the Anglo-Irish chemist had calcined metal. Lomonosov concluded that "the famous Boyle was mistaken" because, he added, "without an excess of external air, the mass of the burnt metal remains the same". Thus, in a chemical reaction occurring in an isolated system, the initial mass of the reactants is equal to the resulting mass of the products formed.



FIGURE 3.15: Mikhail Vassilievitch Lomonosov

Lomonosov was born in the small village of Mishaninskaya in northern Russia, where his father ran a small fishing business. In 1730, at the age of 19, after falling out with his father's third wife, he left his native village for Moscow, where he began his university studies. He was educated at the Slavic-Greek-Latin Academy in Moscow, then at the Kyiv-Mohyla Academy in Kiev and the Academy of St. Petersburg, where he stayed at the same time as the Swiss mathematician Leonhard Euler. From 1736, he spent several years in Germany, where he was associated with the universities of Marburg, Freiberg, and Göttingen, before returning to Moscow in 1741 to join the Physics Department of the Russian Academy of Sciences. In 1743, he was placed under house arrest for eight months after a dispute with his colleagues at the Academy, but resumed his duties in January 1744 after apologizing to those he had offended. A year later, he became a full member of the Russian Academy and a professor of chemistry. He was one of the founders of Moscow State University, which now bears his name.

Often considered one of the fathers of Russian science, Lomonosov is best known for discovering the presence of an atmosphere around the planet Venus, which he observed during a transit of the planet across the disk of the Sun. In a letter to Euler dated July 5, 1748, Lomonosov had already referred to the

principle of conservation of mass, which he believed contributed to the universal laws of nature in the same way as the laws of motion of bodies. He wrote:

> "All the changes taking place in nature are such that every body removed from one is added to another. If matter diminishes in one place, it will increase by the same amount elsewhere; waking hours are taken from sleep."

Before Lavoisier, the Russian scientist rejected the phlogiston theory and promoted the idea of conservation of mass in chemical transformations and physical phenomena. However, his ideas were rejected by German chemists, who remained attached to the phlogiston theory, so the influence of this pioneer hardly extended beyond Russia's borders. Lomonosov, who also wrote poetry, died in St. Petersburg at the age of 53.

Table 3.1: Evolution of chemical nomenclature.

Modern names introduced by Lavoisier	**Former names of chemical species**	**Author**	**Year**
Oxygen (O_2)	Active air or spiritus igneo aerus	Mayow	1668
	Fire air or empirical (imperial) air	Scheele	1771
	Dephlogisticated air	Priestley	1775
	Vital air, eminently breathable gas, acidifying principle or *oxygen* principle	Lavoisier	1777
Nitrogen (N_2)	Air inactive	Mayow	1668
	Exhaust air	Scheele	1771
	Phlogistic or noxious air	Rutherford	1772
	Gaz mofette	Lavoisier	1777
	Nitrogen, nitrogen	Lavoisier	
Carbon dioxide (CO_2)	Spirit or wood gas	Van Helmont	
	Fixed air	Black	1756
	Airborne acid	Black	
	Dephlogisticated air		
	Mephitic acid	Lavoisier	
Hydrogen (H_2)	Terra pinguis	Becher	1667
	Phlogistics	Stahl	1703

The Discovery of Noble Gases

On August 13, 1894, the perpetual secretary of the Académie des Sciences in Paris received a sealed envelope from the Scottish chemist Sir William Ramsay (1852-1916), professor of chemistry at University College, London. Such envelopes, which allow researchers to date a possible discovery, are kept secret for at least 100 years. The one deposited by Ramsay was only opened by the Academy's "Sealed Fold Commission"[111] on June 10, 2004. The document, written in French and entitled *Expériences sur l'azote de l'air*, suggests the presence of a new chemical element in the air. It reads:

> "Guided by an experiment of Lord Rayleigh on the density of nitrogen, which shows that nitrogen obtained from air, by means of metallic copper is heavier by one 231 mi than nitrogen obtained by chemical means from ammonia or azotic acid, I made investigations on the residue [...] started with 20 liters of nitrogen, and after reducing its volume to 200 cubic centimeters, the density increased to 16.1 times that of hydrogen. [...] I hope to be able to decide soon whether this gas is an allotropic modification of nitrogen[112], perhaps Az_3 or a new element."

And Ramsay ends his letter by emphasizing Lord Rayleigh's contribution:

> "In closing this note, it should be noted that it is to Lord Rayleigh, with whom I have been in communication, that we owe this discovery; he showed the place that should be explored; I found the means to isolate this new gas."

In 1894, Sir Ramsay attended Lord Rayleigh's lecture at the Royal Society. Rayleigh pointed out that the nitrogen he had isolated from the air had a density that was not exactly the same as the nitrogen he had produced in the laboratory. The speaker thought he understood the reason for the difference: there were probably impurities in the nitrogen produced in the laboratory. But Ramsay was not convinced. Couldn't there be, as Cavendish thought, other chemical elements in the air that had not yet been identified? The two scientists tried to solve this mystery on their own, but in 1895 they jointly announced in the *Proceedings of the Royal Society* the discovery of a new chemical element characterized by a complete lack of chemical reactivity. They called this gas *"argon*," a name derived from the Greek word εργοσ (energy), preceded by the privative "α". Today, we know that the argon content of the atmosphere is 0.934%.

A year later, in 1895, Ramsay tried to show that the argon source was probably due to the degassing of the Earth's crust. To convince himself, he recorded the spectrum of the gas emitted by a uranium-bearing ore onto which acid had been spilled. To his great surprise, Ramsay found that the spectrum he observed

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[111] Jeannin, Y., Une lettre inédite de Sir William Ramsay sur la découverte de l'argon, *Comptes rendus Chimie, 8*(1), 3-7, 2005, https://doi.org/10.1016/j.crci.2004.11.018.

[112] Ramsay suggested that, if the first hypothesis was correct, the allotropic form of nitrogen N_2 could be a molecule noted Az_3 corresponding to the image of ozone O_3 which is an allotropic form of oxygen O_2.

was exactly the same as that observed by astronomers in the solar atmosphere, which they had named *helium*. The Scottish chemist had thus demonstrated the presence of helium in the Earth's atmosphere. It is said that the excitement of this discovery was so great that Ramsay had to spend a few weeks relaxing in Iceland.

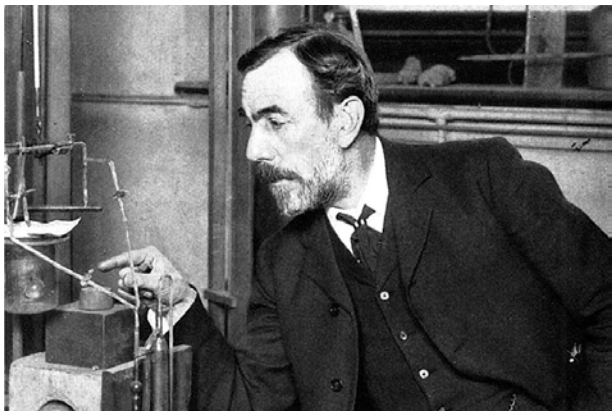


FIGURE 3.16: Sir William Ramsay

In 1898, Ramsay and his University College colleague, the cryogenic chemist Morris William Travers (1872-1961), analyzed the composition of the air they had liquefied using the famous Linde process[113]. This led them to identify the presence of other noble gases in the air, albeit in much smaller quantities: neon, krypton, and xenon. Travers, a Fellow of the Royal Society, was appointed the first director of the Indian Institute of Science in Bangalore, which he led from 1909 to 1914. The discovery of the noble gases earned William Ramsay the Nobel Prize for Chemistry in 1904.

TABLE 3.2: Most abundant gases in the Earth's atmosphere near the surface.

Chemical species	**Proportion in the atmosphere**
Nitrogen (N_2)	78.084 %
Oxygen (O_2)	20.946 %
Argon (Ar)	0.934 %
Neon (Ne)	0.001818% or 18.18 ppmv
Helium (He)	0.000524% or 5.24 ppmv
Methane (CH_4)	0.000072 % or 0.72 ppmv in 1750 0.000180% or 1.8 ppmv in 2010
Krypton (Kr)	0.000114% or 1.14 ppmv
Hydrogen (H_2)	0.000055 % or 0.5 ppmv

Note: 1 ppmv represents 1 part per million by volume.

[113] The process of liquefying air by repeated compression and expansion to produce cooling, used in particular to determine air composition.

Trace Gases in the Atmosphere

It took several centuries to determine with certainty that atmospheric air is a mixture of gases of different chemical natures. Philosophers and naturalists of the time identified various chemical species in the atmosphere that they had observed either by detecting them in the air or by chemically analyzing rainwater collected on the ground. It wasn't until the work of Scottish chemist Robert Angus Smith in 1852 that it became clear that the chemical composition of the air could be altered by human activity, particularly the burning of coal.

Ozone. At the end of the eighteenth century, the molecules identified in the air were oxygen and nitrogen, carbon dioxide, and water vapor. The proportions of these major gases are shown in Table 3.2. A century later, the presence of other chemical constituents, this time in lower concentrations, was observed. These substances included *ozone*, which was discovered in 1839 by Christian Friedrich Schönbein (1799-1868) in Basel, Switzerland, and whose chemical structure (O_3) was not identified until 25 years later by Jacques-Louis Soret (1827-1890) in Geneva (see Chapter 6). In 1858, Jean-Auguste Houzeau (1829-1911), a professor of agronomy in Rouen, France, developed a quantitative method for measuring what he called *odorous oxygen* and discovered that ozone was a persistent gas in the atmosphere. Its concentration was systematically measured between 1877 and 1907 by Albert Lévy (1844-1907) at the Parc Montsouris in Paris.

Hydrogen peroxyde. Another chemical species of particular interest in the nineteenth century was *hydrogen peroxide*[114] (H_2O_2), first produced in 1818 by the French chemist Louis Jacques Thénard (1777-1857) under the name *eau oxygénée*. Its presence in the atmosphere was suggested as early as 1834 by the Scottish chemist William Prout (1785-1850). Laboratory studies of this chemical species were often linked to those of the ozone molecule. In 1858, Schönbein proposed a curious hypothesis: that ozone was actually oxygen with a negative electrical charge, necessarily offset by the positive charge of an oxygenated "counter species" that he called *antozone*. The Göttingen professor of physiology Georg Messner (1829-1905) added that lightning in the vicinity of thunderstorms produced both ozone and antozone, which reacted with cloud water to form hydrogen peroxide. However, it soon became clear that Schönbein's hypothesis had not been verified and was in fact an embarrassing story for the scientists of the time. The story ended in 1879: Antozone was nothing but hydrogen peroxide.

Organic Compounds. During the nineteenth century, several organic compounds were identified in the atmosphere. In 1898, the nutritionist Armand Émile Justin Gautier (1837-1920), professor at the Sorbonne and member of the Académie des Sciences de Paris, observed a gas stagnating over swamps, corresponding to methane (CH_4), the emission of which was first detected in 1778 at Lake Como by Alessandro Giuseppe Antonio Anastasio Volta (1745-1827). More recently, in 1948, spectroscopic measurements of the transmission of solar radiation in the infrared allowed the Belgian Marcel Migeotte (1912-1992) to rigorously identify the presence of this gas in the atmosphere.

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[114] Through the reaction between barium peroxide and nitric acid.

The existence of formaldehyde (H_2CO), another organic compound formed largely by the oxidation of methane, was demonstrated in 1859 by the Russian chemist Aleksandr Butlerov (1828-1886). The species was formally identified in 1868 by August Wilhelm von Hofmann (1818-1892), a professor of chemistry at the University of Berlin. Around 1900, two chemists at the Parc Montsouris Observatory, Henry Henriet, and Albert Lévy, observed the presence of a reducing gas in the air, which they identified as formaldehyde.

In the twentieth century, several other organic compounds were observed in the atmosphere and their concentrations measured at various locations on Earth, including primary hydrocarbons (alkanes, alkenes, terpenes, benzene, xylene, toluene, etc.), carbonyls (aldehydes, ketones), oxygen compounds (esters, alcohols), and organic compounds containing nitrogen, sulfur, or halogen atoms.

Carbon Monoxide. In 1830, the Swiss chemist Nicolas-Théodore de Saussure[115] (1767-1845) suggested that carbon monoxide (CO), a gas identified in the laboratory by Joseph Priestley in the late 18th century, was present in the atmosphere. In 1971, Americans Julian Heicklen (Pennsylvania State University) and Karl Westberg (Aerospace Corporation, California) showed that this gas, previously thought to be quasi-inert, was oxidized by the hydroxyl radical (OH). The concentration of CO was first measured in 1884 by the French chemist Charles-Achille Müntz (1846-1917) and his colleague E. Aubin, working at the *Institut National Agronomique* in Paris.

Hydrogen species. The hydroxyl radical, which is a more powerful oxidant than oxygen, and the peroxyl radical (HO_2) were first studied in the laboratory to estimate their rates of reaction with a variety of chemical species, particularly methane and carbon monoxide. The presence of OH in air was determined in 1924 by spectrometric measurements made by the American William Weldon Watson (1899-1993), an isotope physicist at Yale University who worked on the *Manhattan Project* during World War II. Two years later, British chemist Hugh Stott Taylor (1890-1994), working at Princeton University, suggested that HO_2 must be present in the atmosphere; this radical was detected by mass spectroscopy in 1953 by Samuel Newton Foner (1920-2000), who also worked on the Manhattan Project, and by Richard L. Hudson. Both worked at the Applied Physics Laboratory (APL) of Johns Hopkins University. Systematic measurement of atmospheric concentrations of the two radicals did not begin until the second half of the twentieth century.

In 1957, the Canadian-born American chemist Henry Taube (1915-2005), a professor at the University of Chicago and winner of the 1983 Nobel Prize in Chemistry, proposed that the formation of the OH radical results primarily from the oxidation of water vapor by the oxygen atom in an electronically excited state rather than in its ground state.

The presence of the hydrogen molecule (H_2) in the atmosphere was discovered in 1902 by the British chemist James Dewar (1842-1923) and in 1909 by the French chemist Georges Claude (1870-1960). However, it was P. M. Schuftan

[115] Second son of geologist and meteorologist Horace Bénédict de Saussure (1740-1799), who studied heat exchange in the atmosphere (see chapter 8).

who first determined the abundance of this molecule in the air in 1923. Using measurements taken at the *Linde* Company in Höllriegelskreuth, Bavaria, this chemist showed that the atmospheric concentration of molecular hydrogen was of the order of 0.5 ppm[116]. In an article entitled *The Chemical Composition of the Atmosphere*[117] published in 1937, F. A. Paneth (1887-1958)[118] indicated, based on Schuftan's measurements, that this constituent should play an important role in the stratosphere. In the late 1950s and 1960s, stratospheric concentrations of the two isotopes of hydrogen, deuterium (^{2}H) and tritium (^{3}H), were measured at high altitudes. Deuterium is a stable isotope whose sources are essentially natural, but tritium, a radioactive element, was produced in significant quantities and dispersed into the atmosphere during the American and Soviet thermonuclear explosions of the 1950s and 1960s. The concentration peaks observed during this period were gradually attenuated because tritium has a half-life of 12.3 years.

Nitrogen Compounds. Since the discovery of the nitrogen (N_2) molecule by Daniel Rutherford, Carl Scheele, Henry Cavendish, and Joseph Priestley around 1772, nitrogen compounds have been the subject of much research. Since the studies of John Evelyn in the 17th century, it had been known that rainwater contains "heavenly nitrate", which, according to the Cambridge naturalist John Woodward (1665-1728), is essential for plant growth, an idea proposed as early as 1699 and confirmed in 1836 by the father of agricultural chemistry in France, Jean-Baptiste Boussingault (1802-1887). Twenty years later, in 1856, the French chemist Jules Reiset (1818-1896), a member of the Paris Academy of Sciences, claimed that the decomposition of living matter released nitrogen compounds. It soon became clear that the transformations nitrogen undergoes are part of a biogeochemical cycle essential to life on Earth.

In 1785, C. L. Bertholet pointed out that ammonia, discovered a year earlier by Joseph Priestley, was composed of hydrogen and nitrogen atoms. The history of this gas, synthesized by William Austin in 1887, is interesting because it was already clear at the end of the 19th century that the lack of nitrogen in the soil would make it impossible to feed the world's growing population. In 1909, Fritz Haber (1868-1934), a chemist in Germany, developed a chemical process to produce ammonia, which is needed to make nitrogen fertilizers. His method was adopted by Carl Bosch (1874-1940), who turned it into an industrial process in 1913. It is estimated that today 50% of the world's population benefits from food produced with synthetic fertilizers made by the Haber-Bosch method. For this work, Haber and Bosch were awarded the Nobel Prize in Chemistry in 1918

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[116] Parts per million.

[117] Paneth, F.A., The chemical composition of the atmosphere, *Quarterly Journal of the Royal Meteorological Society, 63*(271), 433-438, 1937.

[118] Friedrich Adolf Paneth was an Austrian-born chemist who graduated from the University of Vienna in 1910. He was a professor at several German universities (Hamburg, Berlin and Königsberg). In 1933, when Hitler seized power, Paneth decided not to return to Germany after giving a series of lectures in England. He became a professor at Durham University. In 1953, he became director of the Max Planck Institute for Chemistry in Mainz, where he became interested in cosmochemistry.

and 1931, respectively. Haber was motivated not only by the threat of famine in Germany in the event of armed conflict but also by the need to produce ammonia for munitions. In any case, this discovery saved billions of lives from starvation worldwide but also led to the extermination of millions of people in the armed conflicts that followed. Today, nearly 100 million tons of nitrogen are used annually as the basic element in agricultural fertilizers, causing major environmental problems such as air pollution and loss of biodiversity.

In 1774, Joseph Priestley discovered nitrous oxide (N_2O), and in 1785, Henry Cavendish discovered nitric acid (HNO_3). Interactions between reactive nitrogen in the atmosphere and the Earth's surface received particular attention at the end of the nineteenth century. The first process to be considered was the fixation[119] of atmospheric nitrogen (N_2) in soils and aquatic systems, a process discovered in 1880 by German chemists Herman Hellriegel (1831-1895) and Herman Willfarth (1853-1904). Several years earlier, in 1877, French agricultural chemists Jean-Jacques Théophile Schloesing[120] (1824-1919) and Achille Müntz had demonstrated the process of nitrification[121]. In 1886, biochemists and agronomists Ulysse Gayon (1845-1929) and Gabriel Dupetit at the University of Bordeaux discovered the process of denitrification[122]. The work of these biogeochemists has led to an understanding of the processes that contribute to the nitrogen cycle throughout the Earth system. In the twentieth century, anthropogenic emissions of nitrogen oxides, primarily from combustion (especially NO), disrupted the natural nitrogen cycle and were a major source of air pollution, acid deposition, and, in many cases, urban ozone formation. When formed in the stratosphere, nitrogen oxides destroy stratospheric ozone. Finally, N_2O contributes to the greenhouse effect in the atmosphere.

Photochemical Smog. All these scientific advances were made by chemists who wanted to better understand the fundamental processes that characterize an atmosphere that is little disturbed by human activity. The appearance of summer smog in the Los Angeles Valley around 1940-1950 opened up a new field of research for this community: understanding how the chemical composition of the air changes under the influence of human activity. The work of

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[119] Microbial action converts nitrogen (N_2) borrowed from the atmosphere into ammonia (NH_3). Inorganic nitrogen fixation enables the biological production of organic nitrogen compounds required for plant growth.

[120] In 1854, the French former students of the Polytechnic School, Théophile Schloesing and Eugene Rolland (1814-1885) developed a chemical process to form soda ash from the reaction of carbon dioxide (CO_2) and sea salt (NaCl) in the presence of ammonia (NH_3). The reaction produces sodium bicarbonate ($NaHCO_3$) and ammonium chloride (NH_4Cl). Soda ash (sodium carbonate Na_2CO_3) is then formed by roasting the sodium bicarbonate. In 1860, Ernest Solvay (1838-1922) took over the chemical process in Belgium and turned it into a large-scale industrial process.

[121] A microbial process in soils by which reducing nitrogen compounds such as ammonia (NH_3) are converted into nitrites (NO_2^-) and nitrates (NO_3^-).

[122] A process occurring in terrestrial and marine ecosystems in the presence of bacteria, by which nitrates (NO_3^-) are transformed into molecular nitrogen (N_2) and, to a lesser extent, nitrous oxide (N_2O). The latter two species are emitted into the atmosphere.

Arie Haagen-Smit, mentioned in Chapter 1, led chemical kinetics specialists to propose chains of chemical reactions leading to the formation of secondary pollutants such as ozone. These included Philip Albert Leighton (1897-1983) at Stanford University, Richard Dunbar Cadle (1915-2010) at the Stanford Research Institute and then at the National Center for Atmospheric Research (NCAR), James N. Pitts (1921-2014) at the University of California at Riverside, Jack G. Calvert (1923-2016) at Ohio State University and then at NCAR, and Harold "Hal" S. Johnston (1920-2012) at the University of California, Berkeley. The chemical chains initiated by the oxidation of carbon monoxide and hydrocarbons involve OH and HO_2 radicals and are directly influenced by the presence of nitrogen oxides (NO and NO_2) in the air, which are very abundant in urban and industrial centers. This work, carried out by laboratory chemists, established the chemical mechanisms that form the basis of the mathematical models used to study and predict air quality.

Air Pollution and Global Change. Since the 1950s, scientists have focused their attention on air pollution, first at the local level, especially in urban areas, then at the regional level, especially in industrial areas, and finally at the global scale. It became clear that air pollution is distributed throughout the planet and affects every region of the world. Since the 1970s, the problem of stratospheric pollution caused by human activities has been raised by the appearance of a *hole* in the ozone layer over Antarctica during the austral spring, which took scientists by surprise. The culprit was identified: chlorofluorocarbons produced by the chemical industry and used in a wide range of applications. Today, questions about the chemical composition of the atmosphere are part of a broader framework of Earth system science that includes assessing the impact of human activities, and specifically the effects of anthropogenic emissions, on the *health* of the planet.

4
Air in Motion

Air is not a static medium. On the contrary, the compressible fluid that surrounds our planet is subject to various forces and thus undergoes complex motions that occur on a variety of spatial and temporal scales. In this chapter, we will trace the evolution of knowledge that led to the emergence of a new discipline: dynamic meteorology. We will see that after centuries of empiricism, meteorology has become a rigorous science that applies the fundamental laws of fluid mechanics to the atmosphere. It uses mathematical concepts and numerical algorithms and takes into account a large number of physical processes, especially those related to changes in the state of water. This science has benefited from advances in basic research initiated by Sir Isaac Newton (1642-1727), more recent technological advances, and especially in the second half of the twentieth century, the launch of satellites for Earth observation.

The motion of air in the atmosphere was already mentioned in Aristotle's treatise *Meteorologica* in the fourth century BC:

> [...] all winds are but one and the same, because air, although in motion, is all one and the same, and if it appears to have any difference, it is only because of the difference in the places from which it flows in all directions.

Aristotle also noted that vertical air motions affect the water cycle in the atmosphere; he wrote in his treatise that

> "The moisture that surrounds the Earth, under the influence of the Sun's rays and the other heat that comes from the sky, vaporizes and rises. But when the heat that caused it to rise runs out [...], the cooled vapor [...] condenses again, and water forms from the air."

Brenda Gardenour Walter[123] sums up Aristotle's view of the role of air in meteorology:

> "Aristotle holds that atmospheric air "surrounding the Earth is moist and warm, because it contains both vapor and a dry exhalation of the Earth"; as the air condenses, it produces clouds, and as it cools, it condenses once

[123] Walter, B.G., Corrupt air, poisonous places, and the toxic breath of witches in Late Medieval Medicine and Theology, in: Fleming, J.R., Johnson, A. (eds.), *Toxic Airs, Body, Place, Planet and Historical Perspectives*, University of Pittsburg Press, 2014.

> "again and turns from air into water. And after the water has formed, it falls again to the Earth" in the form of rain. According to *Meteorologica*, air circulates not only vertically because of continual material transformation and the laws of sublunary physics, but also horizontally because of the spherical rotation of the prime mover, for "it is the revolution of the heaven which carries the air with it and causes its circular motion". Once set in motion, however, atmospheric air does not maintain its circular path, but instead moves erratically across the face of the Earth, a premise proven by the actions of the wind. Aristotle argues that terrestrial winds are not merely atmospheric air in motion, but "Earthy exhalations" that rise from the four cardinal directions, with the north wind, known as the *Septentrio*, being cold and dry; followed by the south wind, or *Meridies*, which is hot and wet; the east wind, *Oriens*, which is cold and wet, and *Occidens*, the west wind, which is hot and dry."

In the second century BCE, the direction of the winds was represented by the deities Boreas (north wind), Cecias (northeast wind), Apeliot (east wind), Euros (southeast wind), Notos (south wind), Lips (southwest wind), Zephyr (west wind), and Sciron (northwest wind) on the magnificent high reliefs of the Tower of the Winds, a particularly well-preserved octagonal building in the Roman Agora of Athens. The direction of the wind was constantly monitored by a weathervane at the top of the tower, represented by a bronze Triton turning on a vertical axis. Theophrastus (c. 372-287 BCE) wrote a *treatise on the winds* that was to be an authority for several centuries.

In the period following antiquity, little decisive progress was made in understanding the mechanisms that govern meteorological phenomena. Although the Arabs revived Aristotle's knowledge in the twelfth century, it wasn't until the fifteenth century, when new continents were explored by sailing ships, that winds were measured. These observations provided information about the motions of air. Two elements were of particular interest to sailors on the high seas. First, the direction and strength of the wind; parameters are essential for maritime navigation. Second, the formation and development of cyclones and storms; these can endanger ships and the lives of sailors.

Atmospheric Circulation

The first major study of atmospheric circulation, specifically the trade winds that converge at the equator but are deflected westward in both hemispheres, was made by the English astronomer Edmond Halley (1656-1742), best known for discovering the comet that bears his name. Halley was interested in the relationship between the distribution of heat from the sun and the motions of air. As Aristotle had pointed out, heated air expands, and as its density decreases, it tends to rise in the atmosphere. This is exactly what happens over the equator, where solar radiation is most intense. To compensate for this vertical movement and to maintain a dynamic equilibrium in the atmospheric motions, there is necessarily an inflow of air at the surface, and thus a movement of colder air masses from higher latitudes toward the equator. The equatorial region, characterized

by upward air motion, cloud formation, and intense precipitation, is now known as the *intertropical convergence zone* (ITCZ). It is sometimes referred to as the equatorial chimney. This convergence zone acts as a kind of barrier, separating the air of the two hemispheres and greatly limiting the exchange between them. Upward movements of air must necessarily be offset by downward movements at higher latitudes.

Halley, who published his study in 1686, added that, if the surface winds heading for the equator are deflected to the west, as the navigators' measurements showed, it is probably because the heat that produces vertical motion follows the sun as it moves from east to west. This idea is similar to that of Galileo, who invoked a delay in the movement of air masses that, once warmed in the tropics, rise in the atmosphere and thus lose contact with the Earth's surface. As for Edme Mariotte, he attributed the westward deviation of the trade winds to variations in the position of the sun in the sky between the equinoxes.



FIGURE 4.1: Edmond Halley (left) and George Hadley (right).

These conclusions were challenged in 1735 by a little-known English lawyer and amateur meteorologist, George Hadley (1685-1768). Hadley confirmed that the air rising over the equator was indeed compensated by a cooler surface current from higher latitudes, but introduced the concept of conservation of momentum according to Newton's laws (to be discussed later in this chapter). This allowed Hadley to invoke the rotation of the Earth, rather than the heat of the Sun, to explain the westward deviation of the trade winds and the eastward deviation of the mid-latitude winds. This concept of planetary rotation added a new and fundamental dimension to the description of atmospheric circulation. Hadley's work was quickly forgotten, however, until the Prussian philosopher Immanuel Kant (1724-1804), a great thinker of the Enlightenment[124], took up

[124] The term "Enlightenment" refers to the development that began around 1700 and aimed to use rational thought to overcome any structures that hindered progress. The goal was to gain acceptance for newly acquired knowledge, such as that produced during the scientific revolution of the 16th and 17th centuries.

the concept to describe atmospheric circulation. Kant, professor of mathematics, physics, and Earth sciences at the University of Königsberg (now Kaliningrad in Russia), published several interesting books: a short work entitled *Neue Anmerkungen zur Erläuterung der Theorie der Winde*[125] in 1756, and a book on physical geography with 17 chapters on the general circulation of the atmosphere. At the end of the 18th century, Pierre-Simon de Laplace and the British meteorologist John Dalton (1766-1844) again demonstrated the role of the Earth's rotation in explaining atmospheric circulation.

George Hadley's most important contribution was the identification of global motions in the atmosphere, manifested by a vast cell between the equator and the poles, with an upward flow of air over the equator, a poleward

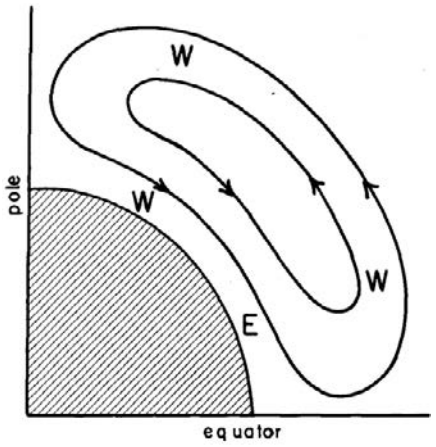


FIGURE 4.2: Cells describing Hadley's meridional general circulation. Source: Lorenz, E.N., A history of prevailing ideas about the general circulation of the atmosphere, History of the Atmospheric Sciences, American Meteorological Society. *BAMS, 64*(7), 1983.

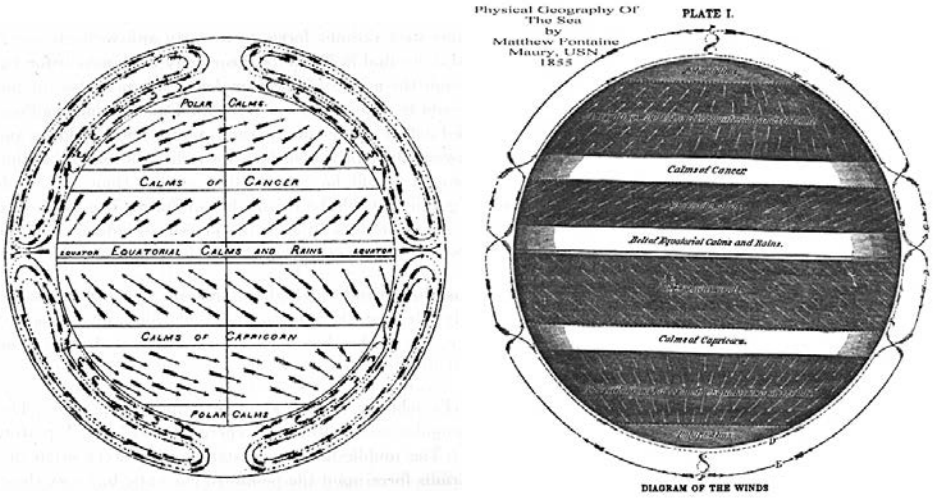
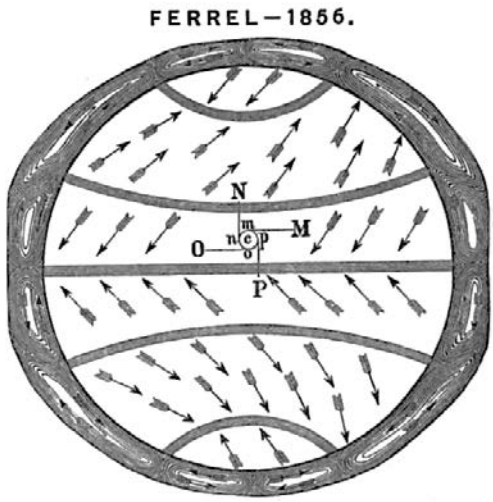


FIGURE 4.3: General circulation proposed by J. Thompson (left) and M. F. Maury (right). Note the existence of several cells describing the mean meridional circulation and complementing the cell proposed by Hadley. Source: Bakerian Lecture: "On the Grand Currents of Atmospheric Circulation" by James Thomson, LL.D., F.R.S., Emeritus Professor of Civil Engineering and Mechanics in the University of Glasgow, March 1892.

[125] "New comments to clarify wind theory".



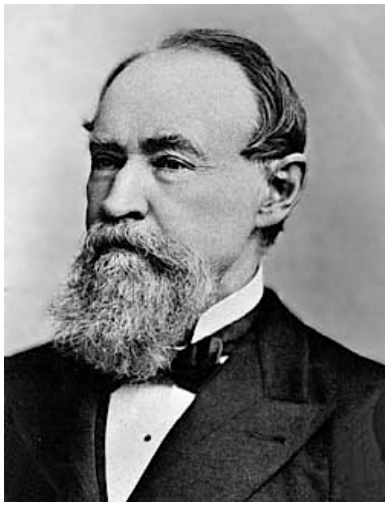


FIGURE 4.4: Left: General circulation proposed by W. Ferrel. Note the existence of several cells describing the mean meridional circulation and complementing the cell proposed by Hadley. Source: Lorenz, E. N., The nature and theory of the General Circulation of the Atmosphere, World Meteorological Organization, Geneva, 1967. On the right, Wilhelm Ferrel.

displacement of air at high altitudes, and a downward flow in the polar regions. The Hadley cell closes in the lower layers of the atmosphere with an equatorward flow. Deviations from these motions are related to the Earth's rotation and explain why the trade winds are deflected westward. Later work, notably by Glasgow professor James Thomson[126] (1822-1892) in 1857 and American meteorologist William Ferrel (1817-1891) in 1859, provided a better description of the meridional atmospheric circulation and showed the existence of other circulation cells that appear at high latitudes. Today, the mean meridional circulation is described by three cells: Hadley's, which extends to latitudes of 30 degrees; Ferrel's, restricted to latitudes between 30 and 60 degrees; and a polar cell found at latitudes higher than 60 degrees.

The boundaries between these cells are characterized by the presence of *jet streams*, which are very strong westerly winds. These currents, whose existence was demonstrated in the 19th century by the American mathematician Elias Loomis (1811-1889), meander around the Earth and promote the eastward movement of storms in extratropical regions. The Japanese meteorologist Wasaburo Oishi (1874-1950), director of the Tateno (now Tsukuba) Aerological Laboratory, was the first to make systematic observations of this phenomenon in the 1920s (see Box 4.1). However, the results of this study were not known in Western countries. The existence of jet streams was rediscovered in 1939 by the meteorologist Heinrich Seilkopf (1895-1968) in Hamburg, Germany. Significant work on the subject continued after World War II, particularly at

[126] British engineer and physicist, born in Belfast, and older brother of William Thomson (Lord Kelvin).

the University of Chicago, under the impetus of the American and Swedish meteorologist Carl-Gustaf Rossby (1898-1957) and the German meteorologist Herbert Riehl (1915-1997). Understanding the characteristics of the jet stream was critical to aviation. To optimize fuel consumption, aircraft flying west avoid jet streams, but benefit from them when flying east.

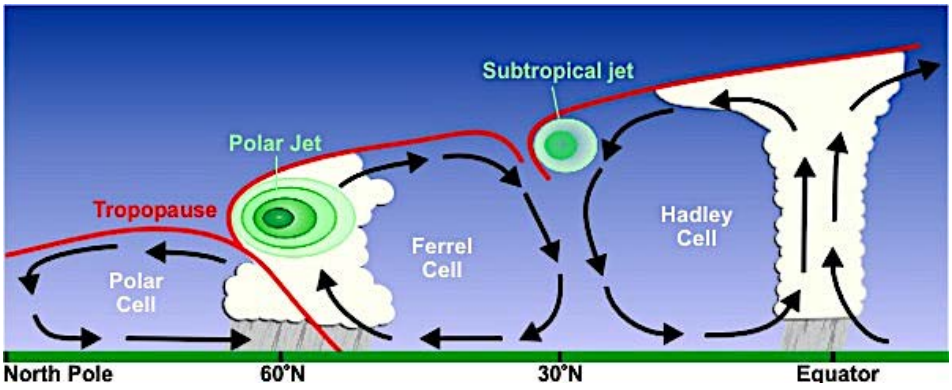


FIGURE 4.5: A contemporary representation of the three cells that characterize the mean meridional circulation in the Northern Hemisphere, with the Hadley cell in the tropics, the Ferrel cell at mid-latitudes and the polar cell at high latitudes. Near the equator, rising air is accompanied by intense precipitation and subsidence around 30 degrees latitude. Near the tropopause and the polar front, the polar jet (intense west-to-east winds) and meteorological disturbances can be seen at around 50-60 degrees latitude. A subtropical jet is visible at around 30 degrees latitude. Source: Geophile Pages.

Box 4.1. The Jet Stream as a Weapon of Intercontinental Warfare.

On this Saturday, May 25, 1945, Reverend Archie Mitchell and his wife Elsie decided to organize a picnic in the forest of Gearhart Mountain with five students from the parish of Bly, a small town in central Oregon, USA. Unexpectedly, in this peaceful setting, a device fell from the sky, exploding violently and killing the small group on the spot, except for the pastor, who was the only survivor. But what had happened? How did this explosive device get to this remote part of the United States?

The balloon-borne incendiary bomb originated on the Japanese island of Honshu. It was developed during World War II as part of an operation known as *Fu-go*, or "wind weapon". At the time, only Japanese scientists and military personnel were aware of the existence of an intense, persistent easterly wind at an altitude of about 10 km that could carry hydrogen-filled balloons from Asia to the North American continent in two or three days.

In the 1920s, meteorologist Wasaburo Oishi (1874-1950) had demonstrated the existence of a strong jet stream over Japan and the Pacific. Oishi, a graduate of Tokyo Imperial University, was hired by the Central Meteorological Observatory of Japan in 1899. From 1911 to 1913 he visited the Lindenberg Observatory near Berlin, one of the most prestigious institutions in the field of upper air meteorology. In 1919 and 1920 he spent several months in the United States, where he brought back modern instruments for observing upper air winds. In 1920 he founded an observatory in Tateno and became its director. It was here that he made systematic measurements of the winds in the air and discovered the existence of the jet stream. This discovery, however, went unnoticed, especially by his American and European colleagues, probably because Oshi, who was also president of the Japanese Esperanto Society, published his work in that language, which is intended to be universal but was not known to members of the international scientific community. His main article was entitled "Raporto de la Aerologia Observatorio de Tateno".

During the Pacific War, another Japanese meteorologist, Hidetoshi Arakawa, made a suggestion to the Japanese military. In an article published in 1956, he wrote:

> "During my stay in Rabaul in the late autumn of 1942, as a sick traveler, I endured the violent bombardments of the Allied air forces. Then I dreamt of attacking the United States with unmanned balloons. Shortly after my return to Japan, I advised the Japanese army and navy through the late Dr. S. Fujiwhara, then director of the Central Meteorological Observatory.
>
> In the meantime, some ten months passed. During this period, the Japanese army and navy had all but given up hope of victory over the Allied forces. To recover from this discouraging situation, the Japanese army adopted my balloon-bomb plan."

Nine thousand balloons were launched between November 1944 and May 1945, but only 300 appeared to have reached their target. Most of the explosives fell in the Pacific, probably because the Japanese meteorologists in charge of the operation overestimated the wind speed at altitude. However, some balloons penetrated deep into American space, reaching states as far away as Michigan. The purpose of these balloons was to cause forest fires and, if possible, destroy vital U.S. installations. The operation was conceived in 1942 in retaliation for the U.S. Air Force's bombing of Japan a few months after the surprise attack on Pearl Harbor in December 1941. The Fu-go program was suspended in April 1945 after the American bombing of Japanese hydrogen facilities.

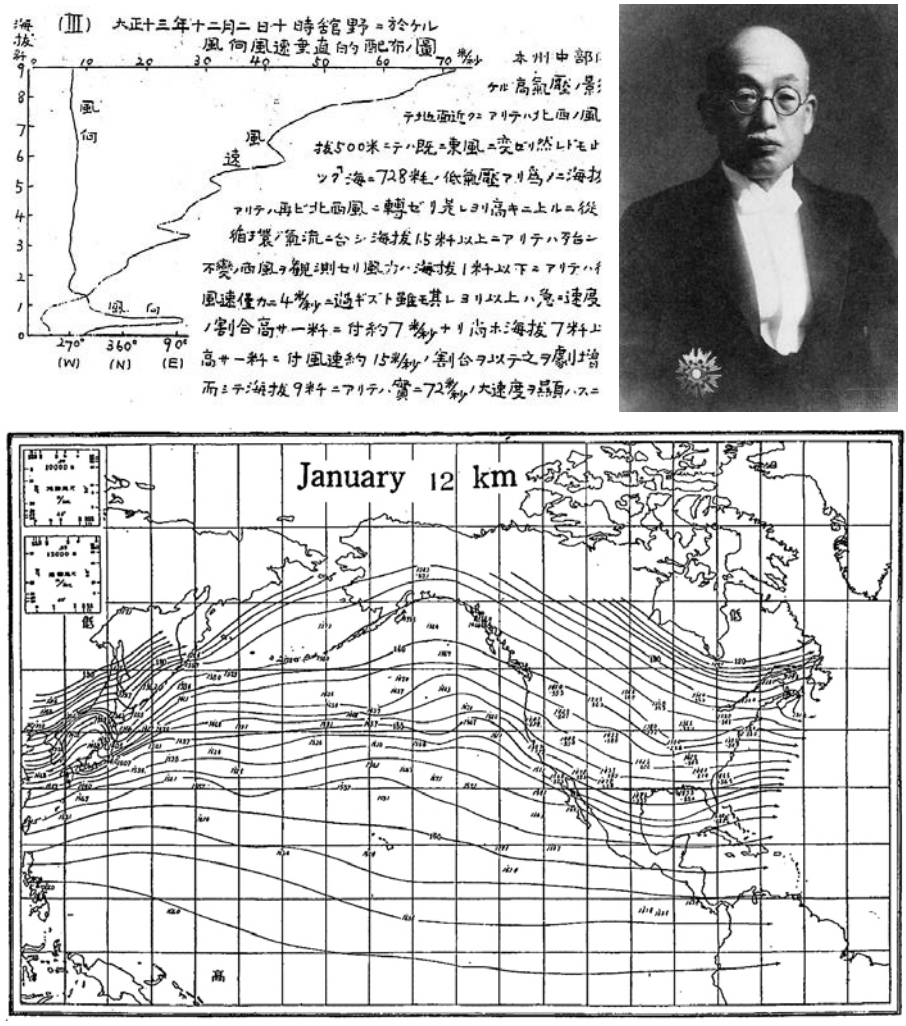


FIGURE 4.6: Top left: Graph showing the vertical distribution of wind direction (approx. 270 degrees) and speed (m s^{-1}) obtained between the surface and 9 km altitude from a balloon launched at Tateno, Japan, on December 2, 2024 at 10 a.m. local time. Top right: Portrait of W. Oishi, circa 1940. Source: Lewis, J., BAMS, March 2003 and Japan Meteorological Agency. Bottom: wind map at 12 km altitude produced by H. Arakawa in January 1945 in support of Operation Fu-go. Source: W. Arakawa, 1956.

The Origin and Trajectory of Storms

Another meteorological factor affecting shipping is the formation of storms that can endanger ships and their crews. This subject was of interest to a British naval officer, Sir Francis Beaufort (1774-1857). Beaufort was a descendant of

the Huguenots, the French Calvinist Protestants who were forced to flee their homeland between the sixteenth and eighteenth centuries to avoid persecution by Catholic governments. He lived and studied in Ireland and Wales until the age of fourteen, when he decided to join the navy to sail the seas. In 1805, this hydrographer, who excelled at charting, drew up a scale that allowed sailors to estimate the effect of wind on sailing conditions. The scale was modified several times before being adopted by the First International Conference on Meteorology held in Brussels in 1853. Subsequent changes were made to reflect the gradual replacement of sailing ships by steam-powered vessels. Today, the Beaufort Scale is widely used to characterize weather conditions at sea and on land. Beaufort continued his career in the service of the British Navy, becoming its official hydrographer and eventually a rear admiral.

In November 1854, during the Crimean War (1853-1856), a violent storm in the Black Sea wiped out thirty-eight ships of the Franco-British coalition fighting Russia off the coast of Sebastopol. Five years later, in October 1859, the steamship *Royal Charter*, sailing from Melbourne, Australia to Liverpool, England, was caught in a storm and smashed against the rocks of Anglesey Island, Wales. Nearly 450 people died in the accident.

Europe was affected by storms like the rest of the world, but the two events mentioned here influenced the development of meteorological services. Two initiatives were taken to prevent similar disasters in the future. In France, the all-powerful director of the Imperial Observatory in Paris, Urbain Le Verrier (1811-1877), pointed out that the trajectory of the Black Sea storm could have been predicted and convinced Emperor Napoleon III to set up a network of observatories to track the movement of cyclones[127] associated with storms. Thanks to the newly installed telegraph, weather reports could be transmitted to Paris and, if necessary, ships warned. This marked the birth of France's first meteorological service, initially based at the Paris Observatory before becoming the *Bureau Central Météorologique* in 1878 and later *Météo-France* in 1993. By the end of 1863, the network included 65 observation stations throughout Europe.

In England, Admiral Robert FitzRoy (1805-1865) took a keen interest in the formation and motions of storms. This British aristocrat enjoyed great authority, having been a member of the House of Commons (1841) and later the Governor of New Zealand (1843-1845). As commander of the ship "The Beagle", he asked Beaufort to find a companion for his voyage who would be an "educated gentleman and close to science". Beaufort suggested inviting Charles Darwin (1809-1882), who would be able to discover several regions of the southern hemisphere. The data collected on this voyage would help establish the famous theory of evolution.

[127] The name *cyclone* was introduced in 1848 by merchant marine captain Henry Piddington to designate an area in which air circulation, often intense, rotates around a center of low atmospheric pressure. Over the oceans, storms occur in these zones, often causing ships to change course. In 1887, Ralf Abercromby drew a distinction between extratropical cyclones and those occurring in the tropics.




FIGURE 4.7: British Admiral Robert FitzRoy (left) and Paris Observatory director Urbain Le Verrier (right).

FitzRoy, eager to predict the arrival of storms, developed meteorological maps that allowed him to better predict the trajectory of cyclones and thus save lives. He coined the term *"forecast*," which is still used in English-speaking countries to describe weather "predictions". He also set up fifteen stations to transmit information by telegraph to London, and established a department responsible for collecting meteorological information on the oceans and sending warnings to ships at sea. This department was the forerunner of the *British Meteorological Office*, now based in Exeter.

FitzRoy was a complex personality who suffered from depression followed by fits of rage, so much so that his nickname among those close to him was "hot coffee". He resented the criticism he received and committed suicide on April 30, 1865, by slitting his wrists in a hot bath. He was 59 years old. In Victorian England, suicide was considered a criminal act, and the person's property was immediately confiscated by the state. Not so for FitzRoy, whose torment was attributed to the difficulty of correctly predicting the weather. One of his biographers, Peter Nichols, writes in *Evolution's Captain*[128]:

> "He made weather forecasts and was publicly ridiculed in the newspapers in the most mocking and humorous terms."

Although the concept proposed by Admiral FitzRoy did not initially receive the attention it deserved, it was eventually adopted by the meteorological services that were gradually being established in most countries.

The First Weather Services

In Europe, under the impetus of the chemist and meteorologist Christophorus Henricus Diedericus Buys Ballot (1817-1890), famous for his law linking wind direction to air pressure gradients, the Netherlands established the Royal Dutch

[128] Nichols, P., *Evolution's Captain, The Story of the Kidnapping That Lead to Charles Darwin's Voyage Aboard the Beagle*, HarperCollins Publisher, 2004.

Meteorological Institute in 1854 and developed a European observation network. This enabled the country to provide the first regular storm warning service in 1861. Weather forecasts were offered to the public in England from 1861 and in France from 1863. In Belgium, under the impetus of Jean-Charles Hippolyte Joseph Houzeau de Lehaie (1820-1888), director of the Royal Observatory, the first weather bulletin based on a synoptic map[129] was broadcast on September 1, 1876. On July 31, 1913, the Weather Service was separated from the Observatory to become an independent institution. In the United States, meteorological stations had been established by the U.S. Army as early as 1816, and major efforts were supported by the *Smithsonian Institution*. The creation of a *National Weather Service* was delayed by the Civil War, but this new institution began operations in 1871 under the responsibility of the *U.S. Army Signal Corps*. The International Meteorological Organization (IMO), which coordinated the exchange of meteorological information, was established in 1880 and replaced in 1947 by the World Meteorological Organization (WMO), a specialized agency of the United Nations based in Geneva, Switzerland.

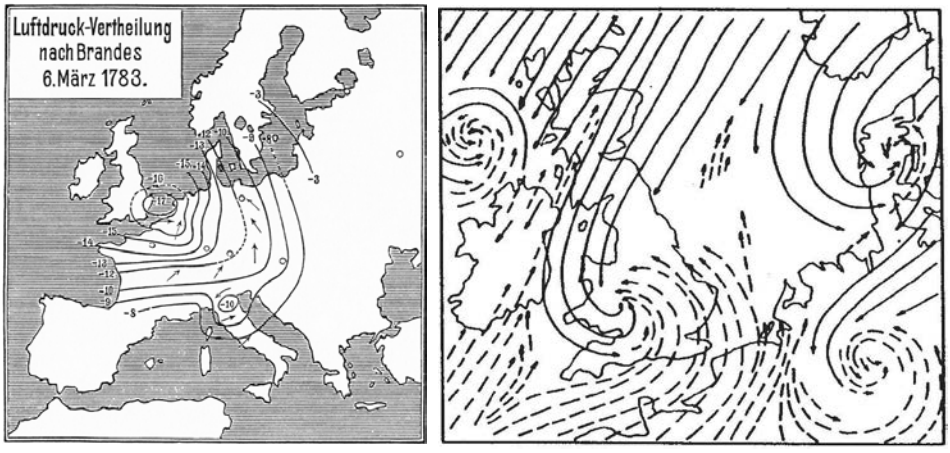


FIGURE 4.8: Left: A reconstruction by Brandes showing the deviation of atmospheric pressure observed on March 6, 1783 from mean pressure, and in particular the existence of a low-pressure area over the English Channel. The direction of wind rotation around the depression is apparent. Right: FitzRoy's map showing the path and meeting of winds from the north (solid lines) and south (dashed lines), and the resulting formation of cyclonic eddies.

Empirical Work

For meteorology, the nineteenth century was a century of trial and error, with only empirical knowledge. The only tools available to forecasters were synoptic maps, which were still imprecise in depicting atmospheric pressure fields on a regional scale, and thus the location of cyclonic zones. In 1820, the mathematician,

[129] Map showing large-scale meteorological phenomena (over 1,000 km) over a vast portion of the Earth's surface.

astronomer, and engineer Heinrich Wilhelm Brandes (1777-1834), professor of physics at the University of Breslau, produced the first weather maps based on information from observation stations in Europe. These maps made it possible to analyze meteorological situations. They were of little use, however, for forecasting on time because the data, which did not yet benefit from the telegraph, arrived several days late. After 1850, weather maps were the only tools available to forecasters. These maps allowed forecasters to track the evolution of low-pressure systems and extrapolate their trajectories for the next few days, taking into account certain empirical laws. The forecasts made little use of the basic laws and theoretical concepts of fluid dynamics already known at the time, so their success often depended on the skill and experience of the forecaster. In the United States, a task force that included meteorologists Cleveland Abbe and William Ferrel called for the weather forecasters of the U.S. Army Signal Corps[130] to take better account of the constraints imposed by scientific knowledge, but this recommendation had little effect. Methodology remained static, and progress was rare. It wasn't until the twentieth century that meteorology became a rational science based on well-established physical principles.

Since ancient times, the appearance of cyclones and storms was most often attributed to a mysterious and malevolent divine action, and it wasn't until the seventeenth century, after the appearance of the first meteorological instruments, that systematic observations were made by sailors on their voyages across the oceans. It was during this period that the first conceptual models of cyclones based on these observations were published. In 1650, the German geographer Bernhardus Verenius (1622-1650) wrote a book[131] that dealt with the question of hurricanes. It wasn't until the 1830s, however, that English sea captain Henry Piddington (1797-1858), who sailed in Asia (India and China), studied the characteristics of tropical cyclones more closely. He took note of the *Law of Storms* formulated by Lieutenant Colonel Sir William Reid[132] (1791-1858) and wrote a book on winds and storms. Reid's law suggests that hurricanes can be described by a large circular motion around a calm zone; indeed, Reid introduced the term *cyclone* to describe this large-scale meteorological phenomenon. However, this description was firmly challenged in 1861 by master mariner G. Jinman[133], who wrote[134]:

> "I assert, and more than that - I will prove it - that there has never been a true circular storm, or what Mr. Piddington and others call a true horizontal cyclone.

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[130] Branch of the U.S. military that manages communications and information systems.
[131] Verenius, B., *Geographia Generalis*, 1650.
[132] Sir William Reid, Scottish military engineer and meteorologist, Governor of Bermuda and Malta.
[133] See Petterssen, S., *Introduction to Meteorology*, McGraw-Hill Book Co., 1941; and Ludham, F.H., *The Cyclone Problem*, Imperial College of Science and Technology, London, 1966.
[134] Jinman, G., *Winds and their courses or A practical exposition of the laws which govern the movements of hurricanes and gales with an examination of the circular theory of storms as propounded by Redfield, Sir William Reid, Piddington, and others*, George Philip and Son, 32 Fleet Street, London, 1861.

Every storm or hurricane has two distinct sides, formed by two distinct currents of air flowing in opposite directions, and intersecting at two points, one on each side of the center: thus a current of air cannot flow in a true circle - it is contrary to reason and common sense to suppose so."

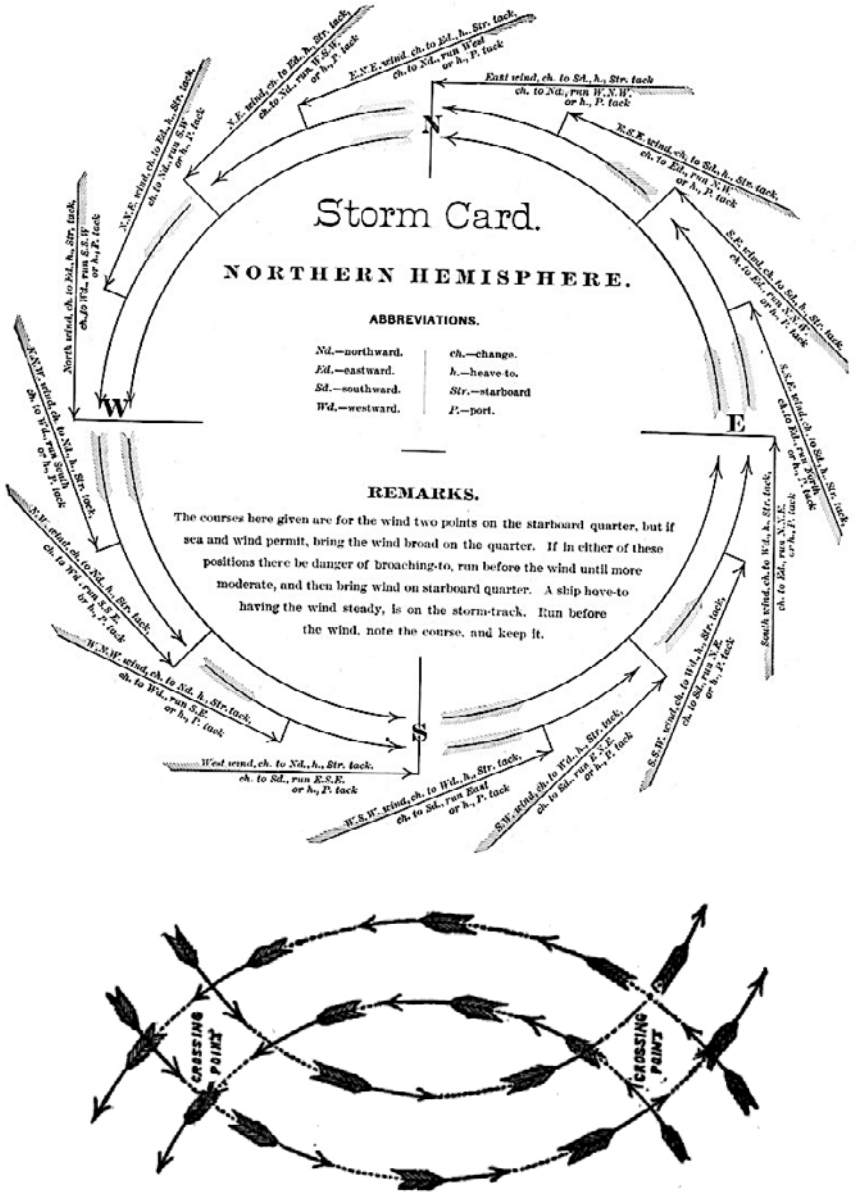


FIGURE 4.9: A description of the airflow around a cyclone ("Laws of Storms", top) from the *Textbook of Seamanship* by Commodore S. B. Luce, US Navy, Von Nostrand Co, New York, 1891 and by description of air movements in the vicinity of a storm by Jinman (bottom).

In his book, Jinman presented an empirical model of an extratropical cyclone in which the surface currents are separated by two confluence lines. He was highly critical of his colleagues, especially the "cabinet philosophers" who developed physical laws without any practical experience at sea.

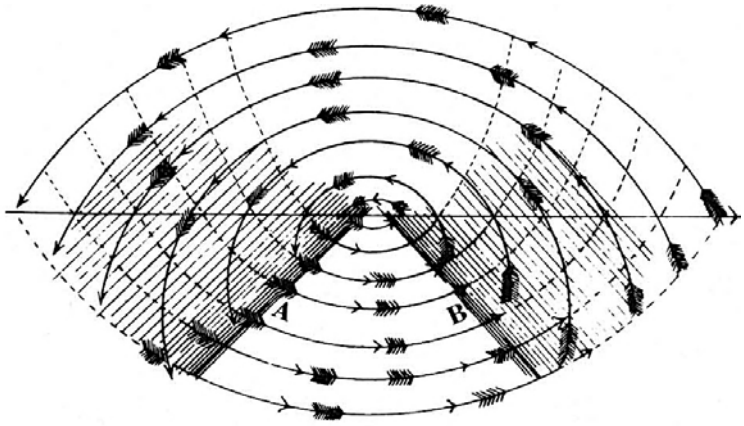


FIGURE 4.10: An early conceptual model of extratropical cyclones from 1861. The author, Master Mariner Jinman, shows air movements and discontinuity lines in wind direction. Source: Jinman, G., *Winds and their courses*, 1861.

Theoretical Work

During the second half of the nineteenth century, the dynamic and thermodynamic mechanisms responsible for cyclone formation were the subject of lively debate and sometimes controversy among specialists. Heinrich Wilhelm Dove (1803-1879), a student of Heinrich Brandes, professor at the Friedrich-Wilhelm University in Berlin, and director of the Prussian Meteorological Institute, often referred to as the father of German meteorology, observed that the winds around low-pressure systems in the northern and southern hemispheres rotated in opposite directions. The American engineer and amateur meteorologist William Charles Redfield (1798-1857), head of the Steam Navigation Company in New York, proposed a *centrifugal theory* of cyclones. The man who became the first president of the American Association for the Advancement of Science (AAAS) in 1848 believed that the circulation of air around low-pressure centers was caused by the forces of gravity and the rotation of the Earth. His kinematic model was based largely on shipboard observations of wind direction, especially in the vicinity of hurricanes, which he considered to be enormous vortices of air. James Pollard Espy (1785-1860), a meteorologist who worked at the Franklin Institute in Philadelphia before joining the U.S. War Department and then the Smithonian Institution in Washington, rejected this view and confronted Redfield directly; in his *thermal hypothesis*, which included convective processes, Espy proposed that convective motions cause air to rise above low-pressure

centers, resulting in a convergence of air at ground level toward the center of cyclones. Thus, it is the rising air that is responsible for water vapor condensation, cloud formation, and precipitation. His thesis, known as the "centripetal motion" of the wind in hurricanes, was published in 1841 in a book entitled *The Philosophy of Storms*. In it, Espy stated that he had no doubts about the relevance of his theory:

> "I have mentioned only a few of the many facts I have been able to gather in favor of a theory that explains, with the simplicity of the law of gravitation, many phenomena that have so far thwarted all attempts at explanation [...]. Enough elements have been presented, however, to establish, beyond any possibility of doubt, the main fact of the theory: the upward movement of air in the region of a cloud at the moment of its formation; and as the explanation of this upward movement is based on facts established by the most meticulous experiments carried out by men such as Black, Dalton, Gay-Lussac, Ure, Bérard and Delaroche, Clément and Desormes, and Petit and Dulong, the theory can claim for itself not only plausibility, but absolute certainty. When the ancients amused themselves by demonstrating the properties of cone sections, they had little thought of the contribution their research would make to the future astronomer. Similarly, the chemists who discovered the latent heat of water vapour and the specific caloric content of atmospheric air could hardly have suspected that their discoveries would soon give rise to a theory of meteorology, explaining so many atmospheric phenomena."

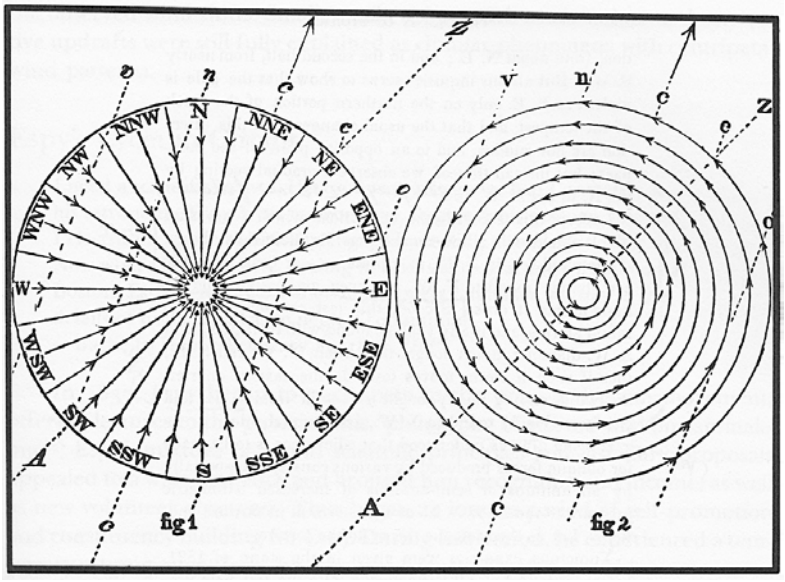


FIGURE 4.11: Two models describing the surface wind around a cyclone: left: James Espy's model; right: William Redfield's model. Source: *Journ. Frankl Inst. 23*, (1839) and J.R. Fleming, Meteorology in America, 1800-1870, The John Hopkins University Press, Baltimore, 1990.

The controversy between Redfield and Epsy intensified between 1834 and 1841[135] with several polemical publications. Things became even more complicated when the chemist Robert Hare (1781-1858), a professor at the University of Pennsylvania, proposed a third hypothesis: cyclones were the result of electromagnetic interaction between two electrically charged "oceans": the celestial ocean and the terrestrial ocean. The electrical force caused by the potential difference between the clouds electrified by the celestial ocean and the surface of the Earth would oppose the force of gravity and, combined with changes in the state of the water, cause the intense air motion that characterizes cyclones. To convince their colleagues of the soundness of their views, the various proponents of the three theories of cyclone formation crisscrossed the United States, and some traveled to Europe to meet with members of the Royal Society in London and the Académie des Sciences in Paris. Astronomer François Arago, puzzled by Espy's remarks in Paris, was quoted as saying: "France has its Cuvier[136], England has its Newton, and America has its Espy."

How does this nearly 30-year controversy end? Certainly, Redfield's centrifugal theory of hurricane wind behavior seemed the most realistic, even if the ideas contained in Espy's thermodynamic theory, particularly those concerning heat exchange in storms, allowed meteorology to move forward. The important point lay elsewhere: the polemic between the two protagonists highlighted two ways of approaching a scientific problem. On the one hand, Espy favored a theoretical approach based on the physical laws known at the time, in a sense adopting the *hypothesis method*[137]. On the other hand, Redfield defined his scientific principles based on a series of observations, in the form of *inductive reasoning* proposed by the English philosopher Francis Bacon. The controversy, which ended successfully for Redfield, had an impact on American research beyond the atmospheric sciences: it strengthened the inductive approach at the expense of the hypothesis method already accepted in Great Britain.

An important step in the theoretical study of cyclone dynamics was taken by Hermann Ludwig Ferdinand von Helmholtz (1821-1894) in 1858. Helmholtz was a great German intellectual who was interested in a wide range of topics, not only in physics and medicine, but also in the philosophy of science, the aesthetics of nature, and the role of science in society. As a professor at the universities of Königsberg, Bonn, Heidelberg, Baden, and finally, at the Humboldt University in Berlin, Helmholtz studied the turbulent motion observed in fluids and emphasized the great stability of this motion. The three important theorems he established taught us that in the absence of viscosity, the intensity of a vortex is invariant over time. In addition, the elements of the fluid (matter)

[135] De Young, G., The Storm Controversy (1830-1860) and its impact on American Science, *EOS, 66*(38), September 17, 1985.

[136] Jean-Léopold Nicolas Frédéric Baron Cuvier (1769-1832), known as Georges Cuvier, French naturalist considered the father of paleontology.

[137] This method is based on (1) the observation and description of phenomena; (2) the development of a hypothesis to explain these phenomena; (3) the forecasting of similar phenomena on the basis of this hypothesis; and (4) the validation of these forecasts by independent experts.

contained within a material contour (e.g., an air filament) surrounding a vortex remain confined within the domain of that contour. The mathematical proof of this theory was given in 1869 by William Thomson (Lord Kelvin, 1824-1907) in the ideal case of a so-called barotropic fluid[138]. Thanks to the Norwegian meteorologist Vilhelm Friman Koren Bjerknes (1862-1951), founder of the Bergen School of Meteorology, Helmholtz's theory was extended in 1898 to the more general case of a baroclinic atmosphere[139]. However, the practical application of this theoretical work to the analysis and forecasting of synoptic situations in the atmosphere was not immediate.

The Bergen School

Around 1920, a small group of researchers in the Norwegian city of Bergen on the Atlantic coast revolutionized meteorology. Vilhelm Bjerknes had just founded an Institute of Geophysics in this charming city, where he applied the rigorous principles of fluid mechanics to the study of atmospheric dynamics. The Bergen School, with the prestigious names of Jacob Bjerknes (1897-1975), Halvor Solberg (1895-1974), Tor Bergeron (1891-1977), Carl-Gustaf Rossby (1898-1957), Erik Palmén (1898-1985), Sverre Petterssen (1898-1974) and Carl Ludvig Schreiner Godske (1906-1970), identified the basic elements for weather analysis and forecasting. Vilhelm Bjerknes established the mathematical basis for rigorous weather forecasting to this day. Vilhelm's son Jacob Bjerknes studied the structure of cyclones. Tor Bergeron became famous for his mechanism on the formation of ice crystals in clouds at the expense of liquid water droplets. Rossby, a student of Vilhelm Bjerknes who attended the University of Leipzig and the Lindenberg Meteorological Observatory in Germany, worked on large-scale atmospheric motions. He is best known for his studies of the propagation of planetary waves, now known as Rossby waves. In 1925, he was awarded a fellowship in the United States, where he first worked for the US Weather Bureau before becoming an associate professor at MIT in 1928. After becoming an American citizen in 1939, he became assistant director for research at the US Weather Bureau. In 1940, he was selected to head the Department of Meteorology at the University of Chicago, where he trained a new generation of meteorologists. He became the first director of the Swedish Institute of Meteorology and Hydrology, dividing his time between Stockholm and Chicago. Palmén, who joined Rossby in the United States, became interested in the dynamics of cyclones and fronts. Petterssen played a crucial role in weather

[138] A barotropic fluid is one in which fluid density is a function of pressure only. In other words, the temperature at a given pressure level is constant. The barotropic approximation was used in the formulation of early mathematical models of the atmosphere, with the aim of simplifying the equations used in these models.

[139] A baroclinic fluid is one in which pressure is not the only factor determining fluid density. This is generally the case in the atmosphere, where air density depends not only on pressure but also on temperature. In this case, lines of equal pressure (isobars) do not coincide with lines of equal density.

forecasting during the Allied landings in Normandy and encouraged General Eisenhower to postpone the military operation from June 5 to 6, 1944. Solberg worked on the theory of tides and atmospheric oscillations. Godske was interested in numerical applications to weather forecasting. In the last years of his life, Rossby was attracted to research topics related to atmospheric chemistry. He saw in this discipline both fundamental questions to be resolved, a relationship to the biogeochemical cycles of carbon and nitrogen, and the possibility of studying the dispersion of chemical species and the lifetime of radioactive tracers from nuclear explosions.

The progress made by the members of the Bergen School was astounding. For example, Tor Bergeron introduced the concept of an air mass[140] which he defined as a quantity of air that covers a large geographic region and whose physical properties are relatively uniform along the horizontal. At the boundaries

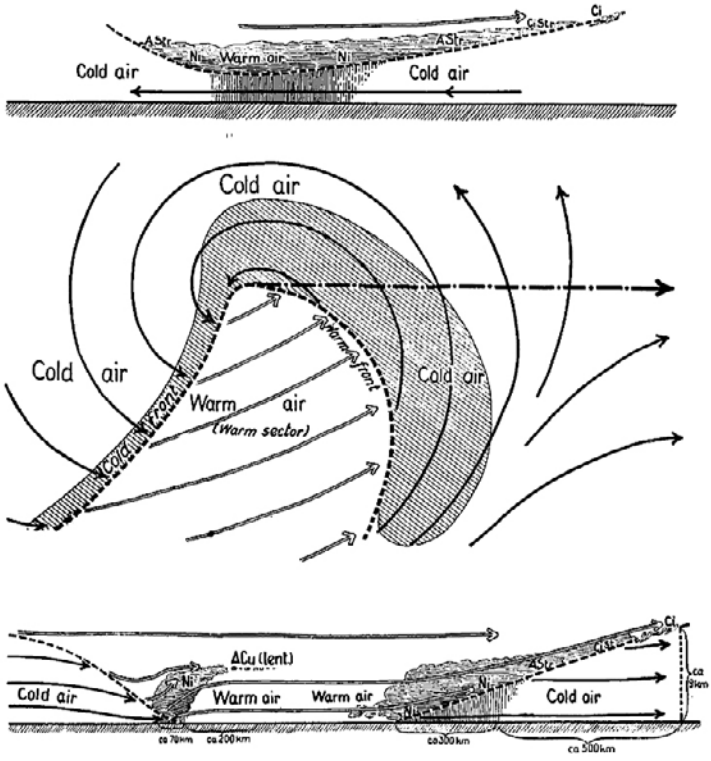


FIGURE 4.12: Description of a cyclone by Jacob Bjerknes in 1919. The surface representation (shown in the center of the drawing) shows the presence of a cold front (Bjerknes calls it a "squall line") and a warm front (Bjerknes calls it a "steering line"). Shaded areas correspond to cloudy and precipitation zones. The upper and lower parts of the drawing show two vertical sections of the cyclone (north and south of the cyclone center). Reproduced from Bjerknes J., Solberg H. Life cycles of cyclones and the polar front theory of atmospheric circulation. *Geofys. Publ., 3* (81) (1922).

[140] Bergeron, T. *Geofys. Publikasjoner, Norske Videnskaps-Akad. Oslo*, V(6), 1928.

of air masses, physical quantities such as temperature and wind speed often change abruptly. These surfaces, known as frontal zones or fronts, were studied as early as 1918 by Jacob Bjerknes and Halvor Solberg, who emphasized the role of the polar front separating polar air masses from subtropical air. Fronts are zones of intense vertical exchange and conversion of potential energy into kinetic energy. Jacob Bjerknes identified the presence of warm and cold fronts in cyclonic systems, separating air masses of different origins. He also described the three-dimensional movement of air near the center of the low-pressure zone and the formation of precipitation.

During this period, the brilliant Austrian meteorologist Max Margules (1856-1920), working at the Central Institute for Meteorology and Geodynamics in Vienna, showed that the difference in potential energy between two contacting air masses of different temperatures was sufficient to produce cyclones. For his theoretical work on fronts, he was awarded the Hann Silver Medal by the Austrian Meteorological Society in 1919, but refused to accept the prize money. With the economic problems and devaluation of the First World War, he fell into poverty and died of starvation a year later.

In Bergen, Jacob Bjerknes and Harvor Solberg[141] showed that cyclones are generated by the development of a wave that generally forms along the polar front. As it progresses, this disturbance intensifies and gradually transforms into an occluded cyclone before finally dissipating and disappearing. This new theory, which describes the life cycle of extratropical cyclones, put an end to the controversy that had always surrounded storm formation. Most importantly, it provided elements that greatly improved the quality of weather forecasting. Mesoscale atmospheric flows[142] associated with disturbances were extensively studied. This was also the case for tropical depressions and hurricanes that develop over the ocean and are particularly devastating when they reach the continent. Robert Friedman's book entitled *Appropriating the Weather*[143] summarizes the development of meteorology in the early twentieth century:

> "The formulation of so-called Bergen meteorology, based on the concepts of fronts and air masses, has long been recognized as one of the principal turning points of this science. The achievements of the Bjerknes group include a new model of the extratropical cyclone, that is, the type of low-pressure system common in the midlatitudes. Claiming that these atmospheric disturbances are composed of three-dimensional surfaces of discontinuities - fronts - the scientists working in Bergen began to conceive of the cyclone as a wave that develops and grows along preexisting polar fronts that separate polar and tropical air masses. [...] Bjerknes' endeavors marked a decisive turning point to a dynamic-physical comprehension of the atmosphere from a statistical-climatological understanding dominant since the late nineteenth century."

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[141] Bjerknes, J., Solberg, H., *Geofys. Publikasjoner, Norske Videnskaps-Akad. Oslo*, III(1), 1922.

[142] Deals with phenomena between the planetary and local scales. By definition, it covers dimensions ranging from a few kilometers to 2,000 km.

[143] Friedman, R.M., *Appropriating the weather; Vilhelm Bjerknes and the construction of a modern meteorology*, Cornell University Press, Ithaca, NY, 252 pp., 1989.

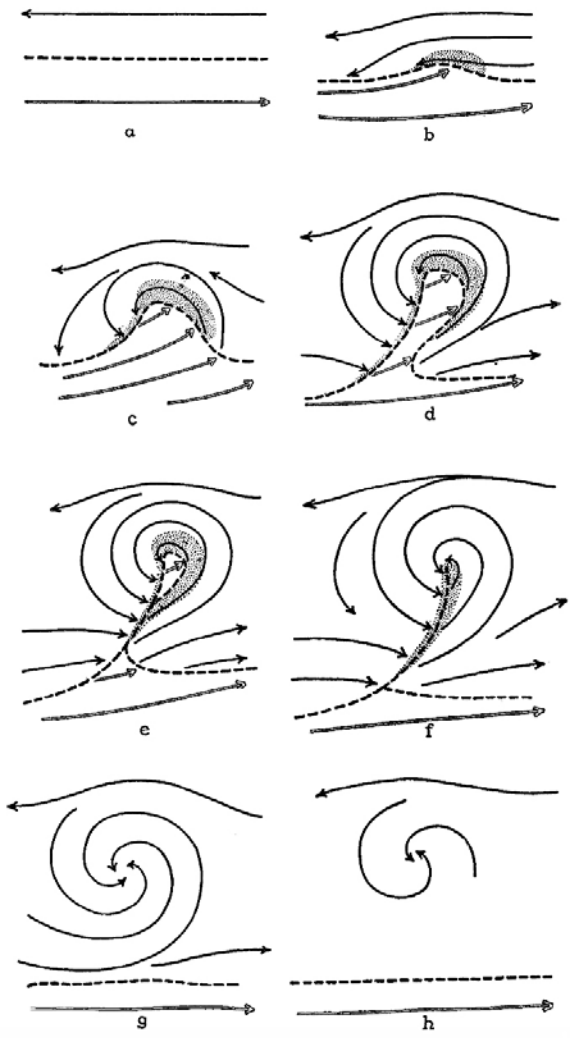


FIGURE 4.13: The life cycle of a cyclone. Reproduced from Bjerknes J., Solberg H., Life cycles of cyclones and the polar front theory of atmospheric circulation. *Geofys. Publ., 3* (81) (1922).

It wasn't until the mid-twentieth century that the Swedish-born American meteorologist Carl-Gustaf Rossby (1898-1957) and the German meteorologist Hans Ertel (1904-1971) established a rigorous mathematical formalism for simulating and thus predicting the formation, motion, and dissipation of cyclonic systems. To exploit the conservation properties of the atmosphere in the absence of heat exchange processes, Rossby proposed to represent large-scale atmospheric flows on isentropic surfaces (surfaces of equal potential temperature[144]) rather

[144] The potential temperature at a point A in the atmosphere is the hypothetical temperature that an infinitesimal element of air would acquire if it were moved from this point A to sea level without any heat exchange (adiabatic compression).

than on isobaric surfaces (surfaces of equal pressure)'. He also demonstrated the conservative nature of a quantity called *absolute* vorticity[145], which accounts not only for the vorticity of the atmosphere but also the effect of the Earth's rotation. Ertel, who worked at the Prussian Meteorological Institute before joining the University of Innsbruck in 1943 and the Free University of Berlin in 1946, generalized Rossby's theory and introduced the concept of *potential vorticity*[146] in 1943. He showed that in the absence of dissipation processes, this atmospheric variable is conserved as a function of time on an isentropic surface. Thus, if an air element retains its potential temperature, it also retains its potential vorticity. This latter quantity, which contains information about wind speed, can therefore be thought of as a dynamic tracer that is conserved as it moves through the atmosphere. Thinking in terms of vortices to describe atmospheric dynamics offered a new perspective for describing air motions in the atmosphere and was therefore an important new development for studies in theoretical meteorology. The recognition of the stability of vortex circulation in the atmosphere by Helmholtz, Kelvin, and Bjerknes, and the development of mathematical formulations based on the vortex concept, allow us to better anticipate the evolution of vortex systems, and in particular that of cyclones and related storms.

Thus, after a period dominated by empiricism, theoretical meteorology really took off in the early to mid-twentieth century, becoming a true scientific discipline based on the laws of fluid dynamics and thermodynamics. The work of Sir Isaac Newton (1642-1727) in the seventeenth century formed the basis for the rational development of the atmospheric sciences.

Newton's Laws

To attempt a rigorous study of atmospheric circulation and to establish a mathematical formalism capable of predicting the evolution of meteorological systems, we must first refer to the laws of mechanics established by Newton in his book *Philosophiae Naturalis Principia Mathematica* (better known as *"Principia"*), published in 1687. This masterpiece of scientific literature was written in Latin and translated into French in 1723[147] and then into English[148]

[145] The "vorticity" is a vector quantity that describes the local rotational motion of a continuous medium (such as air) near a certain point in the fluid. Mathematically, it is defined as the rotational velocity of the fluid. The "absolute vorticity" of an air particle is the sum of the vorticity imparted to this fluid particle by the flow of the continuous medium surrounding it, and the vorticity imparted to it by the rotation of the Earth's surface.

[146] The "potential vorticity" is defined as the scalar product of the vorticity and the fluid stratification (expressed as the vertical gradient of the potential temperature divided by the air density).

[147] Translated into French as "*Principes mathématiques de philosophie naturelle*" by the French writer and physicist Gabrielle Émilie Le Tonnelier de Breteuil, Marquise du Châtelet (1706-1749). Émilie du Châtelet, who had a long relationship with Voltaire, introduced Leibniz's works to France.

[148] Translated into English by the mathematician Andrew Motte (1696-1734), brother of the London publisher Benjamin Motte (1693-1738) who published the translation.

in 1729, is also a difficult document to read because it relies on considerations of Euclidean geometry rather than more contemporary algebraic formulations. Newton's writing of this treatise was the result of a long process that began in 1684 when the astronomer Edmond Halley visited the Cambridge physicist to share the results of his work. This work suggested that the gravitational force exerted by the Sun on the planets was inversely proportional to the square of the distance between the two bodies. Halley asked Newton if he could calculate the orbit of the planet that would result from this law of attraction. A few months later, Newton sent Halley a document entitled *De motu corporum un gyrom* (On the Motion of Orbiting Bodies), in which he developed the theoretical elements that explained the empirical laws established a few years earlier (1609-1619) by the German astronomer and mathematician Johannes Kepler (1571-1630), and in particular why the orbits of the planets must be elliptical. Newton's work on celestial mechanics formed the basis of the universal theory of gravitation that would revolutionize astronomy. The *Principia* generalized these conclusions, presenting the fundamental principles of body dynamics and a description of the system that governs the universe. The Royal Society, in financial difficulties at the time, was reluctant to publish the work, but with Halley's support, it was finally published in 1687.

In his *Principia*, Newton established the three laws of motion that still form the basis of classical mechanics. The first of these laws states that the motion of a body does not change unless a force is applied to it. This law expresses *the principle of inertia*[149]. The second law, known as the *law of motion*, states that the change per unit of time in the momentum of a body[150] is equal (in direction and magnitude) to the force applied to it. This fundamental principle of dynamics states that if the mass of a body is invariant, the acceleration it undergoes is proportional to the force applied. Thus, a force changes the velocity and possibly the direction of displacement of the body to which it is applied. Finally, the third law states that when two bodies interact, they exert equal and opposite forces on each other. This is the law of *action and reaction*, which is particularly important for calculating the trajectories of celestial bodies. It was therefore Newton's theory that enabled Le Verrier to discover the existence of the planet Neptune orbiting the Sun by calculation alone, prompting the French physicist Arago to say that "Neptune was discovered with the tip of a pen".

Newton was elected a Fellow of the Royal Society in 1672 at the age of 26. His personality was complex, and his relationships with his colleagues were often difficult. However, he also demonstrated extraordinary intellectual creativity in the field of mathematics. His work on calculus provided a powerful

[149] The first expression of the principle of inertia is due to the French philosopher, astronomer, mathematician and Catholic priest Pierre Gassendi (1592-1655), who wrote as early as 1642 in his work *De motu impresso a motore translato* (Louis de Heuqueville, Paris, 1642) that, unless prevented from doing so, any body set in motion in any direction continues to move along a straight trajectory.

[150] The momentum of an object is the product of its mass and velocity. It is a vector directed in the same direction as the velocity vector.

mathematical tool for tackling mechanical problems. It was also the source of a long and intense dispute with the German philosopher and mathematician Gottfried Leibniz (1646-1716), who was working on the same issues. Leibniz was also a member of the Royal Society, which was called upon to mediate the conflict between the two figures. The illustrious society, which Newton had chaired since 1703, eventually ruled in favor of the English scientist, much to the anger of Leibniz, who considered the arbitration biased. A few years earlier, Newton had clashed with the astronomer Royal John Flamsteed (1646-1719) over the publication of a catalog of stars. Newton was also accused of plagiarism by a scientist close to the chemist Robert Boyle, Robert Hooke (1635-1703), also a member of the Royal Society. Hooke claimed to have discovered the laws of universal gravitation before Newton. Another confrontation between the two scientists arose from their work on the colors of light.

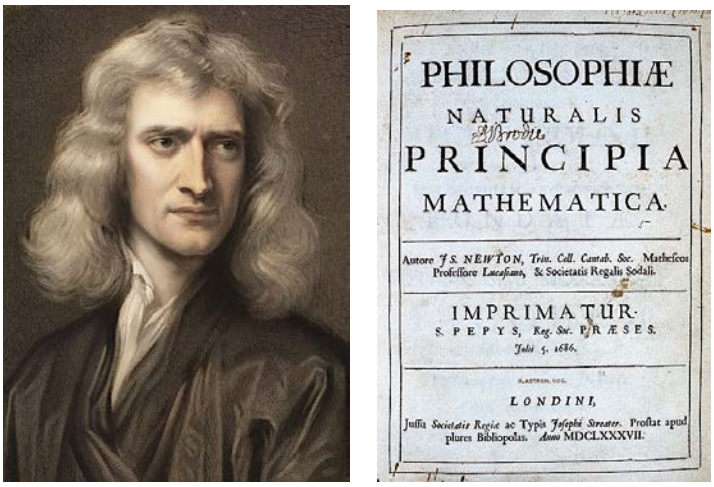


FIGURE 4.14: Isaac Newton (left) and his book *Principia*, which presents the fundamental laws of classical mechanics (right).

The Determinism of Newton and Laplace

When he wrote his laws in 1666, Newton was aware of Galileo's measurements of falling bodies[151] from the Leaning Tower of Pisa (1602) and Kepler's observations (1609 and 1619) of the motion of orbiting bodies. The universal laws resulting from this work are deterministic since they allow us to calculate very precisely the motion of a body whose initial conditions and forces are known. These laws truly revolutionized science because they suggested that the evolution of the world could be predicted and that all the world's problems could be solved.

[151] Galileo's law states that the duration of the fall of a body is independent of its mass, and is proportional to the square root of the height from which the body falls.

For example, in 1814, Pierre-Simon de Laplace, an adept of causal determinism, wrote in the introduction to his *Essai Philosophique sur les Probabilités*[152]:

> "We must, therefore, consider the present state of the universe as the effect of its former state, and as the cause of that which will follow. An intelligence which, at a given moment, knew all the forces with which nature is animated, and the respective situations of the beings which compose it, if it were, moreover, vast enough to submit these data to analysis, would include in the same formula the movements of the largest bodies in the universe and those of the lightest atom: nothing would be uncertain to it, and the future, like the past, would be present to its eyes."

According to Laplace, the universe functions like a finely tuned mechanism, making it possible, for example, to accurately describe and predict not only the trajectories of the planets but also the behavior of the Earth system. A deterministic system is inherently predetermined and therefore predictable. This idea was shared by the German geographer and explorer Alexander von Humboldt (1769-1859), who wrote in his 1846 book *Kosmos* that the structure of the universe could be reduced to a simple problem of mechanics. Humboldt, who traveled the world, clearly understood the importance of the interactions between the various components of the Earth system and the need for a holistic vision of the world that unites the various scientific disciplines. For many philosophers of the time, even atheists like Laplace, determinism was proof of the existence of a supreme intelligence that enjoyed absolute power and controlled the evolution of the universe.

Considered one of France's most illustrious scientists - sometimes called the French Newton - Laplace began his career in Paris in 1769. This protégé of Jean Le Rond d'Alembert, editor with the philosopher Denis Diderot (1713-1784) of the famous *Encyclopédie*, was interested in Newton's work, especially the laws that explain the orbits of celestial bodies. He was also inspired by the work of Leonhard Euler[153] (1707-1783) and Joseph-Louis Lagrange (1736-1813). Laplace's early work was so well received that he was elected to the Académie Royale des Sciences in 1776 at the age of 27. In the following years, Laplace worked on the orbits of the planets and the stability of the solar system; in particular, he attempted to solve the *three-body problem* by finding approximate solutions to the differential equations describing the motion of

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[152] Philosophical Essay on Probability.

[153] Leonhard Euler is considered one of the greatest mathematicians in history. The Swiss scientist, logician, astronomer and engineer began his studies at the University of Basel at the age of 13. His dissertation in 1723 for his *Magister Philosophiæ* was a comparison of the philosophies of Descartes and Newton. In 1727, he joined the Imperial Russian Academy of Sciences in St. Petersburg, where he worked with the Swiss mathematician Daniel Bernoulli (1700-1782). In 1741, he left Russia for Berlin but returned to St. Petersburg 26 years later in a Russia now ruled by Empress Catherine II (1729-1796) after the coup d'état she staged against her husband Emperor Peter III (1728-1762). Euler is known for his work in analytic number theory, complex analysis, infinitesimal calculus, graph theory and topology.

these bodies. In 1776, he also presented a mathematical study of the tides and developed a theory of probabilities that would be the subject of several publications. However, his scientific career was interrupted by a series of political events that changed the fate of the world. Laplace witnessed the collapse of the *Ancien Régime* and, beginning in 1789, the advent of the French Revolution. These events did not prevent him from being appointed a member of the *Commission des Poids et Mesures* in 1790 and, like his fellow academicians, from participating in some of the events of the Revolution. However, he was excluded from this commission when the Académie des Sciences was closed in 1793. During the Terror (1793-1794), Laplace left the turbulent and dangerous scene of Paris to take refuge with his family in Melun. In 1795, when the situation had stabilized, he returned to Paris where he helped establish the *Institut de France* (the new Académie), the *École polytechnique* and the *École normale supérieure*. In 1799 he published his *Traité de Mécanique Céleste*. He also witnessed the rise to power of Napoleon Bonaparte (1769-1821), who made him his Minister of the Interior after the coup d'état of 18 Brumaire. Laplace remained in office for only six weeks because, as Napoleon wrote during his exile: "he was a more than mediocre administrator" who "had only problematic ideas and carried the spirit of the infinitely small right into the administration". Often described as opportunistic and, according to the director of the Paris Observatory, Jérôme Lalonde (1732-1807), insolent and malicious, this personality was made a Count of the Empire in 1806. With the restoration of royalty in 1814, he swore allegiance to the House of Bourbon and became a Marquis of the Kingdom of France in 1817.



FIGURE 4.15: Alexander von Humboldt (left) and Pierre Simon de Laplace (right).

Atmospheric Dynamics Equations

Laplace's concept of causal determinism encouraged scientists to express the fundamental laws of physics in rigorous mathematical equations that could, in principle, predict physical quantities and their evolution as a function of time at any point in space. When applied to a fluid (such as air), Newton's second law of motion states that the acceleration experienced by a fluid element of infinitesimal volume[154] (called a *fluid parcel*) multiplied by the density of the fluid equals the sum of the forces applied to that element. This involves identifying all the forces involved (such as gravity and the effects of pressure gradients) that determine the trajectory of each element.

Box 4.2. Atmospheric Governing Equations

Atmospheric airflow simulation is based on the resolution of a system of partial differential equations. These express in mathematical form the fundamental laws of physics applied to a compressible fluid (air).

To determine the equation that expresses Newton's second law applied to atmospheric fluid whose mass density (kg of air per cubic meter) is denoted ρ, we first take into account the force that tends to homogenize the fluid by reducing pressure differences within it. This force and the resulting displacement of air elements are directed from high-pressure zones to low-pressure zones. The corresponding force is therefore proportional to the spatial pressure gradient $(-\nabla p)$ within the fluid. This gradient results for example from inhomogeneities in the heating of air masses. Secondly, we take into account the friction forces (F) between neighboring elements within the fluid; these dissipation processes affect the speed of motion of the various air elements, and their formulation is not always obvious. By definition, in a so-called Newtonian fluid (which applies to air), the shear stress inside the fluid is a function of the velocity $\boldsymbol{V}$ of the elements in the fluid, with a constant of proportionality μ which is characteristic of the nature of the fluid and is called dynamic viscosity. Finally, we consider the gravitational force ($\rho \boldsymbol{g}^*$), which acts on the fluid in a vertical direction (towards the center of the Earth). Taking these different forces into account, we can write the momentum equation, the solution to which gives us the three-dimensional velocity field $\boldsymbol{V}$ of the air in the atmosphere:

$$\frac{d\boldsymbol{V}}{dt} = \frac{\partial \boldsymbol{V}}{\partial t} + (\boldsymbol{V}.\nabla)\boldsymbol{V} = \boldsymbol{g}^* - \frac{1}{\rho}\nabla p + \boldsymbol{F}$$

where $d\boldsymbol{V}/dt$ represents the acceleration undergone by an element of air. Vectors (defined by amplitude and direction) are denoted by bold symbols. In a Newtonian fluid, the dissipation force is proportional to the Laplacian

[154] This element is small enough to be assimilated to a point, but large enough to possess mass, volume and temperature.

of the velocity: $\boldsymbol{F} = \nabla.(\mu\nabla)\boldsymbol{v} \cong \mu\Delta\boldsymbol{V}$ so the equation is a second-order partial differential equation. Note in the above equation that the material derivative $d\boldsymbol{V}/dt$ has been decomposed into a local acceleration $\partial\boldsymbol{V}/\partial t$ and a so-called advective acceleration $(\boldsymbol{V}.\nabla)\boldsymbol{V}$. The latter term highlights the nonlinear nature of atmospheric dynamics and the complexity of the flows that occur on different space and time scales.

When used to characterize meteorological fields in a reference frame linked to the Earth's surface, this equation must be modified to take into account the effects of the Earth's rotation. The velocity described by the vector $\boldsymbol{V}$ which appears in the above equation actually represents the speed relative to an inertial reference frame (linked, for example, to the center of the Earth) and not the speed (notated $\boldsymbol{v}$) as perceived by an observer linked to the Earth's surface. To determine the acceleration undergone by this observer, we now express the equation of momentum in a rotating reference frame linked to the Earth's surface. In this case, the equation of momentum is written as

$$\frac{d\boldsymbol{v}}{dt} = \frac{\partial\boldsymbol{v}}{\partial t} + (\boldsymbol{v}.\nabla)\boldsymbol{v} = -2\Omega\times\boldsymbol{v} + \boldsymbol{g} - \frac{1}{\rho}\nabla p + \boldsymbol{F}$$

where the factor Ω represents the angular velocity of the Earth's rotation. In other words, when expressed in the reference frame attached to the Earth's surface, the equation contains an additional term $-2\Omega\times\boldsymbol{v}$ which represents an *apparent* Coriolis force, linked to the Earth's rotational speed. The additional effect of the centrifugal force resulting from the Earth's rotation is expressed by a vector directed perpendicular to the Earth's axis of rotation. This is usually combined with the gravitational vector $\boldsymbol{g}^*$ to form a resultant vector $\boldsymbol{g}$ which represents *apparent* gravity. When the dissipation term is expressed by the viscosity term specific to Newtonian fluids, the above equation is called the Navier-Stokes equation. When this term and the effect of gravity are ignored, we refer to *the Euler equation.*

The law of conservation of energy, known as the "first law of thermodynamics", makes it possible to determine the temperature in the atmosphere by solving the equation

$$C_p\frac{dT}{dt} = C_p\left(\frac{\partial T}{\partial t} + (\boldsymbol{v}.\nabla)T\right) = Q + \frac{1}{\rho}\frac{dp}{dt}$$

This equation expresses that the change in temperature of the atmospheric fluid $\partial T/\partial t$ at a fixed point in the fluid is determined by the net rate of heating Q resulting from the absorption of solar radiation or the emission and absorption of atmospheric radiation, as well as the heat released by changes in the state of water in the atmosphere. Temperature change also results from the work $(1/\rho)\,dp/dt$ to the fluid in the form of compression or expansion, and finally the transport of heat $(\boldsymbol{v}.\nabla)T$ due to atmospheric circulation. In this expression, C_p refers to the heat capacity of air (1005 J kg^{-1} K^{-1}). The interaction between solar and terrestrial radiation and the atmosphere depends essentially on the presence in the air of gases such as ozone, water vapour, carbon dioxide and other less abundant molecules. Determining the Q term therefore requires precise calculation of radiative transfer in the atmosphere.

Conservation of mass is expressed by the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho \boldsymbol{v}) = 0$$

Finally, the perfect gas equation links pressure, density and temperature.

$$p = \rho R T$$

where R (287.04 J kg^{-1} K^{-1}) represents the perfect gas constant.

From these equations, we derive the following quantities in the spatial domain under consideration: air density, pressure, temperature and the three components of fluid velocity. An additional equation expressing the water vapour balance, taking into account evaporation and condensation processes, determines the spatio-temporal distribution of air humidity. The atmospheric distribution of chemical species is calculated by solving a system of continuity equations that take into account the effect of a multitude of chemical reactions. These equations are generally non-linear, and their resolution requires powerful numerical computing resources.

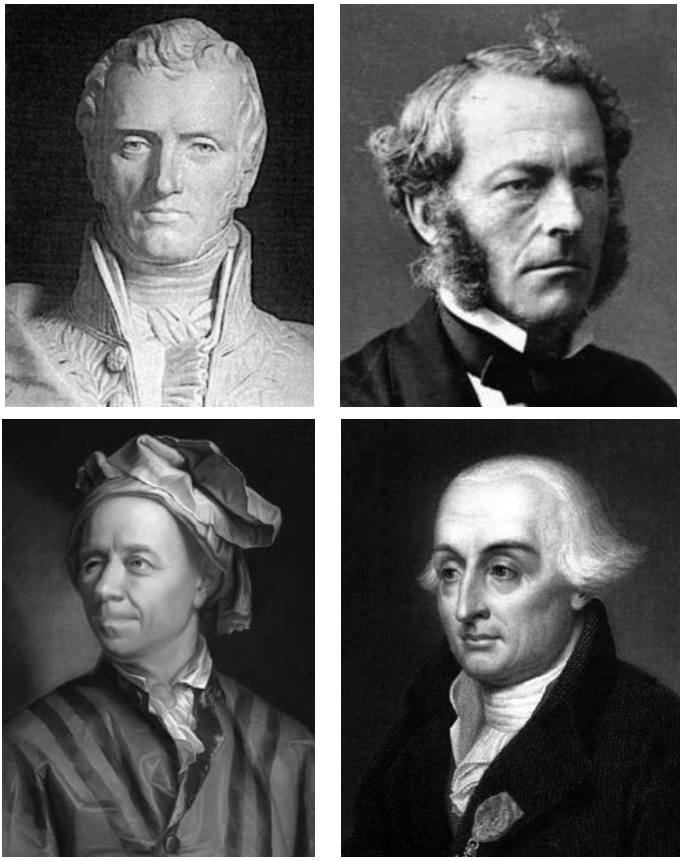


FIGURE 4.16: Above: Claude-Louis Marie Henri Navier (left, bust at the École normale des Ponts et Chaussées), George Gabriel Stokes (right). Below: Portraits of Leonhard Euler painted in 1753 by Emmanuel Handmann and exhibited in the Kunstmuseum Basel (left) and Joseph-Louis Lagrange (right).

When applied to the atmosphere, the momentum equation, which expresses Newton's second law, can be used to determine three-dimensional wind speed fields as a function of pressure gradients, taking into account the effect of gravity and of Earth's rotation. However, it must be supplemented by additional differential equations expressing other physical principles: conservation of mass and conservation of energy. The first of these, which expresses the indestructibility of mass and makes it possible to calculate air density, states that at any point in space, the convergence of air motions leads to a local increase in air density, while divergence causes a local decrease in density. The second equation expresses one of the laws of thermodynamics formulated in the 19th century by the German physicists Rudolf Clausius (1822-1888), Hermann Ludwig von Helmholtz (1821-1894), the British physicists James Prescott Joule (1818-1889) and William Thomson (Lord Kelvin) (1824-1907). Applied to the atmosphere, it states that the local change in temperature as a function of time is determined by the input or loss of energy due to the absorption of solar radiation, the emission of terrestrial radiation, the energy released or absorbed during changes in the state of water, and the heat transport associated with atmospheric circulation. Finally, the law of perfect gases establishes a relationship between atmospheric pressure, density, and temperature.

The brilliant Swiss mathematician Leonhard Euler (1707-1783) established a special form of the momentum equation that applies to the flow of a non-viscous, adiabatic fluid (no energy exchange with the environment, so no dissipation effects). He considered that it is the pressure variations that generate fluid motion. Therefore, at any point in a fluid, the product of the density and the acceleration of a parcel of air is proportional to the pressure gradient. On this basis, he derived the famous Euler equation mentioned in Box 4.2.

In this description, the motion of the fluid is observed from a fixed point in space. Joseph-Louis Lagrange used a different formulation; in his method, he followed the motion of each element of the fluid along its trajectory. The analogy of a boat moving along a canal clearly distinguishes the two approaches: in Euler's formulation, the observer stands on the canal bank and watches the boat move; in Lagrange's formulation, the observer stands on the boat and watches the banks pass by. Other scientists, including Daniel Bernoulli (1700-1782), Jean d'Alembert (1717-1783), and Pierre-Simon de Laplace, were also interested in the motion of so-called perfect fluids.

These early studies overlooked an important property of fluids: their viscosity. This was already mentioned by Newton, who wrote in his *Philosophiae Naturalis Principia:*

> "The resistance that arises from the diminishing slippery nature of the parts of the fluid, all other things being equal, is proportionate to the rapidity with which the parts of the fluid are separated from each other."

Observation shows that many fluids, including air, behave according to Newton's principle. These are known as Newtonian fluids. In 1821, the French physicist Claude-Louis Navier (1785-1836) introduced the concept of fluid viscosity (friction) into the equation of momentum. The Anglo-Irish physicist Sir George Gabriel Stokes (1819-1903) studied the motion of particles in viscous

fluids. The Navier-Stokes equation is a generalization of the Euler equation. It allows us to address issues related to turbulent flows in fluids and, in particular, to study the nonlinear interactions that exist between dynamical structures in the fluid characterized by different spatial and temporal scales. It also takes into account an important external force: gravity.

The Navier-Stokes equation, established in the nineteenth century and consisting of partial derivatives of order two, is particularly difficult to solve. Its integration must be based on numerical methods that benefit from the use of electronic computers; we had to wait for the development of powerful computers to satisfactorily simulate the flows of compressible fluids such as air and to take into account the interactions between dynamical structures of different sizes that characterize turbulence.

Claude-Louis Navier (1785-1836), who specialized in the mechanics of continuous media and in particular in the mathematical theory of elasticity, was an engineer who graduated from the École Polytechnique in Paris (1802). He became a member of the Académie des Sciences (1824) and a professor at the École des Ponts et Chaussées (1830). Because of the high standard of his work on structural analysis, he was commissioned to build several bridges and footbridges in France, including the Pont des Invalides in Paris. However, after this prestigious work was completed, cracks appeared in the structure of the bridge, which had to be dismantled and rebuilt. Overconfident in his theoretical calculations, Navier ignored the need for safety margins, earning him a reprimand from the government.

George Stokes (1819-1903), Professor at Cambridge University (1849) and Fellow of the Royal Society (1851), presented his law of viscosity in 1851 in a paper that has remained famous ever since. Because of his marriage to Mary Susanna Robinson, he lost his fellowship at Pembroke College, Cambridge (reserved for unmarried men), but regained it in 1862 when the rules of the college were changed.

When applied to the Earth's atmosphere, the Navier-Stokes equations must account for the rotation of the planet. Newton's laws were established in an inertial reference frame, i.e., one that is fixed relative to a reference frame outside the Earth. If we want to express atmospheric quantities as perceived by an observer on the Earth's surface, we must apply a transformation to the equations that reveal the so-called apparent forces, whose amplitude is determined by the Earth's rotational velocity and is a function of latitude. This force, already emphasized by George Hadley to explain

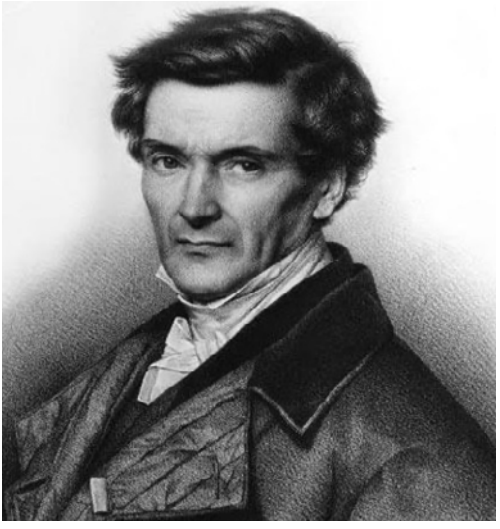


FIGURE 4.17: Gaspard-Gustave Coriolis.

the trade winds, was formalized in 1835 by the French engineer[155] Gaspard-Gustave Coriolis (1792-1843) in an article entitled *Sur les équations du mouvement relatif des systèmes de corps.* The Coriolis force is responsible for the deviation of winds to the right in the Northern Hemisphere and to the left in the Southern Hemisphere. It also explains the clockwise circulation of air in the Northern Hemisphere around high-pressure areas (anticyclones) and the counterclockwise circulation around low-pressure areas. In the Southern Hemisphere, the situation is reversed.

For a complete representation of atmospheric phenomena, we need to add to the mathematical system an equation that describes the evolution of humidity, taking into account both the transport of water vapor and the changes in state between the liquid, solid, and gaseous phases. Many of the physical processes involved in the formation and dissipation of cloud systems, as well as evaporation and precipitation processes, come into play here. Finally, equations expressing the conservation of mass of different chemical species, taking into account their atmospheric transport and the chemical transformations they undergo, are used to determine the distribution of chemical constituents in the atmosphere. These various coupled equations form the basis of mathematical

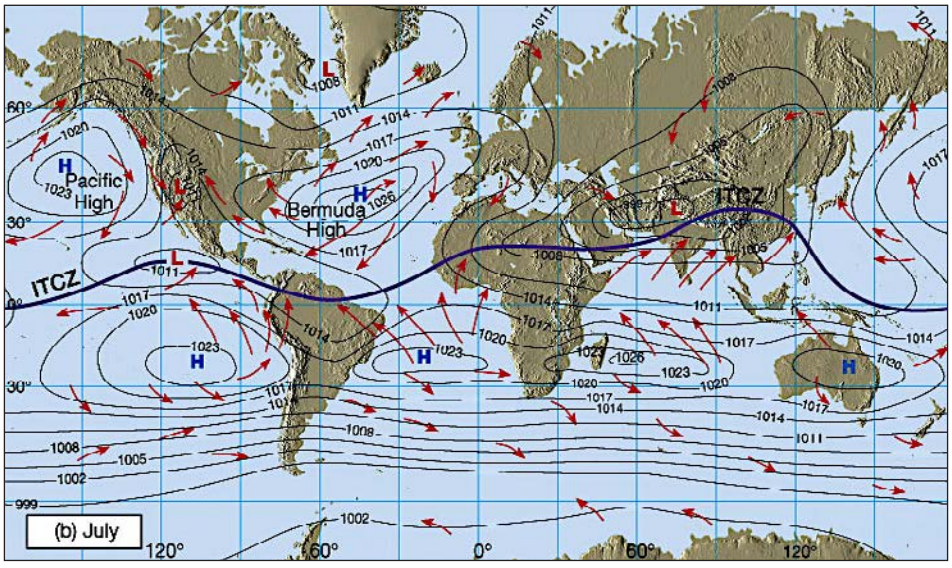


FIGURE 4.18: Global climatological distribution of surface air pressure in July. Shown in bold is the Intertropical Convergence Zone (ITCZ), which is characterized by convergence of horizontal winds and strong updrafts associated with intense precipitation and severe thunderstorms. High pressure zones are visible in subtropical regions and are characterized by dry air descent and areas of good weather. The wind direction indicated by the arrows is influenced by the pressure field and the apparent Coriolis force, which takes into account the Earth's rotation. Winds blowing north in South Asia form the summer monsoon, which is associated with heavy rainfall. Source: Lutgens, K. and Tarbuck, E.J. *The Atmosphere. 8th Edition*, Prentice-Hall, Upper Saddle River, NJ, 512 p, 2001.

[155] *Journal de l'École Royale Polytechnique 15*, 144-154, 1792-1843.

models of the atmosphere. These models are used to predict weather and air pollution; coupled with ocean and continental models, they allow us to project future climate trends. The system of equations for atmospheric dynamics is nonlinear, so finding solutions requires the use of complex numerical methods.

The First Numerical Weather Forecasts

The concept of causal determinism introduced by Laplace had a considerable influence on the thinking of nineteenth-century meteorologists. The implementation of the concepts introduced by Newton and translated into the Euler and Navier-Stokes equations was intended to allow rational prediction of the evolution of meteorological systems over relatively long periods of time. Until then, weather forecasting had relied on empirical methods, often based on observation. But by applying the laws of physics, forecasting became a truly scientific process.

The Norwegian physicist Vilhelm Bjerknes (1862-1951), whose work was mentioned earlier, developed a methodology that became the basis for numerical weather prediction. This scientific personality was encouraged by his father, the mathematician and physicist Anton Bjerknes (1825-1903), who taught fluid mechanics at the University of Christiana (now Oslo) and passed on his passion for mathematical physics to his son. In Bonn in 1890-1891, Vilhelm Bjerknes was a student, then assistant, of the German physicist Heinrich Rudolf Hertz (1857-1894), a leading specialist in the propagation of electromagnetic waves; he was therefore well acquainted with Maxwell's famous equations, from which he drew inspiration for his formulation of theoretical meteorology. Bjerknes saw a certain similarity between the equations used to calculate electric and magnetic fields and the equations of hydrodynamics. Inspired by the work of the Swedish oceanographer Vagn Walfrid Ekman (1874-1954) and his student, the Swede Carl-Gustaf Arvid Rossby (1898-1957), Bjerknes, who taught at Stockholm University (1895-1906), was convinced (as was Laplace) that by solving the equations relating to atmospheric currents, it must be possible to calculate temperature, pressure, and wind fields, provided that the initial values of these physical quantities are known. It should therefore be possible to apply the laws of hydrodynamics to the problems faced by meteorologists. In a famous article published in 1904, Bjerknes presented a plan to help meteorological services improve the quality of their weather forecasts. Using medical vocabulary, he argued that it was necessary to *diagnose* the present state of the atmosphere in order to *predict* its future state. He wrote[156]:

> "If, as anyone interested in science believes, atmospheric conditions develop according to natural laws from the preceding situations, it follows that the necessary and sufficient conditions for a rational solution of the problems of weather forecasting are as follows:
>
> 1. The state of the atmosphere must be known at a specific time with sufficient accuracy;

[156] Bjerknes, V., Das Problem der Wettervorhersage, betrachtet vom Standpunkte der Mechanik und der Physik. *Meteorol. Z.*, 21, 1-7, 1904.

2. The laws which determine the development of a meteorological condition from another condition must be known with sufficient precision."

He concluded his article:

"The most important task [...] of theoretical meteorology will ultimately be to take this picture of the state of the atmosphere as a starting point and construct future states [...]. Comparison of the states constructed with those observed will, on the one hand, partly enable the validity of the methodology to be verified, and on the other hand will provide indications for better values of constants and for improvements in the technique."

In 1907, Bjerknes returned to the Royal Frederick University in Oslo, and in 1912, he became a professor of geophysics at the University of Leipzig in Germany, before moving to Bergen in 1917, where he founded the Institute of Geophysics (1917-1926). He also helped found the famous School of Meteorology, which had a major influence on the development of weather forecasting techniques in the early twentieth century. He was elected a member of the Royal Swedish Academy of Sciences and a Fellow of the Royal Society. His son, the meteorologist Jacob Bjerknes (1897-1975), worked in his father's group in Leipzig and later in Bergen. In particular, he studied the dynamics of the polar front. In 1940, he emigrated to the United States and founded the Department of Meteorology at the University of California, Los Angeles.

In the United States, meteorologist Cleveland Abbe (1838-1916) was also a proponent of predicting the weather by mathematically solving hydrodynamic and thermodynamic equations, as illustrated in his 1901 article "The physical basis of long-range weather forecasting".

Vilhelm Bjerknes never attempted to solve the equations of dynamics and thermodynamics of the atmosphere himself. It was Lewis Fry Richardson (1881-1953), a British meteorologist, who undertook this task. Richardson was interested in numerical techniques for finding approximate solutions to differential equations, especially when analytical solutions could not be found. In 1913, he



FIGURE 4.19: Vilhelm Bjerknes.
Painting by Rolf Groven

joined the *British Met Office* as "superintendent" of the *Eskdalemuir Observatory* in Scotland, where he began to develop a method for solving these equations. In 1916, at the time of World War I, Richardson, a Quaker who had become a conscientious objector, left this institution to join an ambulance unit of the religious society of Friends. His duty was to transport wounded soldiers during the hostilities to the Belgian city of Ypres. Despite the very difficult and dangerous conditions he had to face, especially during the Battle of Champagne in April 1917, Richardson used his free time to continue his work as a meteorologist. To find the solution to the equations describing atmospheric movements, he covered the map of Europe with a kind of chessboard of squares on which he calculated the value of atmospheric variables, particularly pressure and wind speed. For each square on the chessboard, Richardson replaced the differential equations with a system of algebraic equations. At a chosen time (May 20, 1910, 7 a.m. Universal Time) and for each of these chessboard squares, he assigned initial values for each atmospheric variable based on available meteorological observations. He then began solving the equations by hand to determine the weather six hours later. Due to the enormous number of mathematical operations required to complete the forecast, it took him six weeks to determine the solution of the equations and to produce a 6-hour forecast at a single geographic location. Richardson's method is described in a book entitled *Weather Prediction by Numerical Process*, published in 1922, which is one of the best works on the subject.

Richardson's predictions did not match the observations. They thus disappointed meteorologists like Bjerknes and Abbe, who had pinned their hopes on a rational approach to weather forecasting. However, it is not only the numerical method used that is to blame, but rather the inconsistencies in the initial conditions assumed. The solution obtained was unrealistic because the lack of equilibrium between the initial values of the various meteorological variables had generated large oscillations in atmospheric pressure. In the model, this last quantity increased by 145 hPa in 6 hours, while the observed pressure remained practically unchanged during this period. This problem was solved in the following

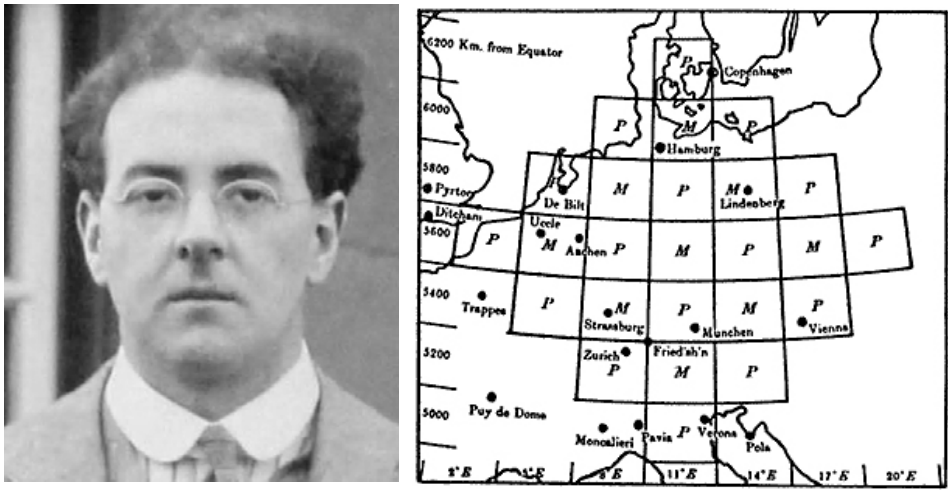


FIGURE 4.20: Left: Lewis Fry Richardson. Source: BBC. Right: Richardson's digital grid covering part of Europe.

years, citing the need to filter out the "noise" generated by the model[157], which was the source of instability in the calculation. Despite this setback, Richardson's work established meteorology as a quantitative science and paved the way for the weather forecasting methods still used today.

In his attempt to predict the evolution of the state of the atmosphere, Richardson recognized a practical difficulty: because the numerical operations had to be performed manually, in the absence of electronic calculators, it took several weeks to predict the evolution of the meteorological situation for a period of only 6 hours. The calculation process had to be speeded up. Richardson proposed a solution: get a large number of people together to do the calculations in parallel. He envisioned setting up a large theater, which he described as follows:

> "Imagine a large hall like a theatre, except that the circles and galleries go right round through the space usually occupied by the stage. The walls of this chamber are painted to form a map of the globe. The ceiling represents the north polar regions, England is in the gallery, the tropics in the upper circle, Australia on the dress circle and the Antarctic in the pit. A myriad computers [people who compute] are at work upon the weather of the part of the map where each sits, but each computer attends only to one equation or part of an equation. The work of each region is coordinated by an official of higher rank [...].
>
> Four senior clerks in the central pulpit are collecting the future weather as fast as it is being computed, and dispatching it by pneumatic carrier to a quiet room.
>
> In a neighboring building there is a research department, where they invent improvements. But there is much experimenting on a small scale before any change is made in the complex routine of the computing theatre. [...] In another building are all the usual financial, correspondence and administrative offices. Outside are playing fields, houses, mountains and lakes, for it was thought that those who compute the weather should breathe of it freely."

In describing his hypothetical weather forecasting factory of 64,000 people working in parallel, Richardson offers a startling perspective for those who will design the massively parallel processors used in modern computers at the end of the twentieth century.

After the end of hostilities, Richardson returned to the British Met Office. But true to his pacifist convictions, he resigned in 1920 from this institution, which had just become part of the Air Ministry and was therefore under military control. He then taught at various English colleges and was elected a Fellow of the Royal Society in 1926. During this time, he became interested in the problem of turbulence in the atmosphere. After 1935, however, he turned his attention to other matters, developing mathematical theories to explain human conflicts and their degeneration into war. Meteorological forecasts played a major role during the Second World War (Boxes 4.3 and 4.4).

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[157] In other words, to filter out the stochastic disturbances superimposed on meteorological quantities, whose amplitude, if it increases as a function of time, is a source of numerical instability.

Box 4.3. German Secret Weather Stations During the Second World War

With the many air and naval operations that took place during World War II, weather forecasting played an important role in military mission planning. These forecasts were based on a thorough knowledge of current weather conditions, which required the collection of data over a large geographical area. Since the weather in Europe is highly dependent on the arrival of disturbances that form and develop over the American continent, the North Atlantic, and the Arctic, it was crucial to have information from these areas. While important data, particularly for forecasting the arrival of storms and other weather disturbances, was transmitted by ships, submarines, and aircraft en route to the Atlantic region, these sources of information became increasingly uncertain as the fighting intensified. To remedy this situation, the German army (Wehrmacht) decided to secretly install weather stations in several areas controlled by their enemies, particularly in Greenland and on the North American continent.

Greenland Weather Stations

Several German weather stations were established on the east coast of Greenland. On August 22, 1942, the meteorological ship *Sachsen* arrived in Hansa Bay off Sabine Island with a group of meteorologists led by Gottfried Weiss and a Wehrmacht unit commanded by Lieutenant Hermann Ritter. The ship's passengers disembarked to set up a military-guarded observation station called *Holzauge*. It regularly reported weather data to the Third Reich's forecasting services.

On March 8, 1943, a patrol of three Norwegian and Danish policemen and trappers, known as the *Sledge* Patrol, set out for Sabine Island. The men knew of a cabin on the coast, but as they approached, they noticed smoke coming from the chimney and footprints in the snow. Two men fled from the cabin, where the patrol found Nazi weapons and uniforms. They had just discovered the presence of German meteorologists and soldiers who had settled in the area. They decided to return to their base in Eskimonaes, about 100 km to the south, but stopped at a nearby cabin to spend the night with the sled dogs before continuing their long journey. A few hours later, several men approached the cabin. Fortunately, the darkness allowed the Danish-Norwegian patrol to leave. However, they were forced to leave some of their equipment and dogs behind. Exhausted and starving, the three men managed to reach the Eskimo base a few days later.

But the incident was not over. On March 25, the dogs at the Eskimo base began barking loudly. Footsteps could be heard on the ice. The Germans asked to talk to the people on the base. One of them agreed to let one of the German soldiers come closer as long as he dropped his gun. The German lieutenant asked, "Will you use force if we don't accept your conditions?" And the Dane answered: "*Jawohl*". The Germans responded immediately by opening fire but allowed the three Danes and two Greenlanders inside the base to escape to the south. The Eskimo base was then set on fire by the soldiers who returned to the weather station on Sabine Island.

At the time of this incident, two members of the sledge patrol had gone north to retrieve one of their own who had been confined to a cabin on Sabine Island and return him to the Eskimonaes base before he was discovered by the Germans. Unexpectedly, however, the three patrol boats bound for Eskimonaes encountered the German soldiers returning from their punitive expedition. German Lieutenant Ritter ordered his men to shoot at the sled dogs, but a bullet hit one of the sled patrollers, who died half an hour later. He was the only Greenlandic casualty of the military conflict. The other two men were captured and taken to the station on Sabine Island. One of them, however, managed to escape on a sled after being allowed to bury his comrade, who had been shot by German soldiers. The second, during a moment alone with Lieutenant Ritter, managed to disarm him and take him to the Scoresly Sound station (Ittoqqortoomiit). He was turned over to the Americans as a prisoner of war and interned in the United States until the end of hostilities. The Wehrmacht weather station on Sabine Island was bombed and destroyed by American aircraft in May 1943; the German personnel was evacuated by a German Dornier DO-26 aircraft in June 1943.

Further Attempts to Install German Stations

Two islands in the Arctic were considered suitable for the installation of weather stations. The Germans, having learned that the inhabitants of Spitsbergen had been evacuated from the island, sent a group of 10 meteorologists to collect data important for weather forecasting in Europe. A hastily constructed airstrip in the northeast of the island allowed the air force to bring in scientific equipment and supplies. Information about the state of the atmosphere was regularly transmitted by radio until June 1942, when Norwegians supporting the Allies landed on the island. The Norwegians searched for the Third Reich men, but they were nowhere to be found. They had been rescued and evacuated by submarine, but left behind an automatic station on Spitsbergen that transmitted weather data throughout the summer of 1942.

The island of Jan Mayen, halfway between Norway and Greenland, was also coveted by the German military. Only four Norwegian meteorologists were present on this small island of volcanic origin, whose largest dimension was no more than 20 km. As soon as they heard by radio that their country had been conquered by Hitler's troops, they decided to send their data to London rather than to German-occupied Oslo. To prevent the men from falling into German hands, a Free Norwegian gunboat set sail for Jan Mayen, but crashed on a reef off the coast. While waiting to be rescued, the 68 crew members stranded on the island were forced to subsist on seal meat and polar bears, which were fortunately in the area. A British ship picked up the sailors and meteorologists.

Realizing that the island was now deserted, the Germans decided to send meteorologists and soldiers in the *Sonderkommando Finkenstein*, named after its aristocratic leader, Count Ulrich von Finkenstein. However, the trawler Heinrich Frieese, which was taking the commando to its destination, was chased by a British cruiser, and in its haste the German ship crashed into the

rocks of the island. Two German passengers drowned; the others were taken prisoner by the British. Allied forces retook the island in March 1941, despite repeated bombing by Luftwaffe aircraft from occupied Norway. The Germans eventually relinquished possession of the island, which remained in Allied hands until the end of the war.

These difficulties did not prevent the German authorities from ordering the establishment of other weather stations in the Arctic. One of them, called *Bassgeiger* Station, was established on Shannon Island in the summer of 1943, but was also discovered by a Sedge patrol. After a short battle and the death of one German soldier on April 22, 1944, it was evacuated in June 1944. Finally, the German stations *Edelweiss* I and II in northeastern Greenland were seized during raids by U.S. Army patrols in September and October 1944.

A German Automatic Weather Station in North America

Two German submarines (the U-boats U-86 and U-537) were designed to carry installations that could be used as weather stations in various parts of the world. The first was of little use; it was sunk by the British Royal Air Force off the coast of Norway in 1944. The second was of greater service to the meteorologists of the Third Reich.

On September 18, 1943, the submarine U-537, captained by Lieutenant Schrewe, set sail from Kiel in northern Germany for the Labrador Peninsula in the independent Dominion of Newfoundland, now part of Canada. On board were two meteorologists working for Siemens: Kurt Sommermeyer and his assistant Walter Hildebrand. The voyage was difficult: the submarine was caught in a heavy storm and hit an iceberg; it was damaged but reached its destination. It was anchored in Baie Saint-Martin. While sailors attempted to repair the damage to U-537, the equipment, including powerful nickel-cadmium batteries and the radio transmitter, was landed on dinghies and installed in an uninhabited area on the northern tip of the peninsula. The station, with its ten 1-meter-high cylinders and two masts of 4 and 10 meters, was named KURT, after the meteorologist in charge of the mission. To cover their tracks, the Germans affixed a "Canadian Meteor Service" logo to the equipment. They also scattered opened packs of American cigarettes around the station. This expedition was the only one in which Nazi German military personnel set foot on the North American continent. Once the installation was complete, the submarine returned to Europe, receiving signals from the automatic station on a frequency of 3940 kHz every three hours. On December 8, 1943, it reached the Wehrmacht occupied port of Lorient, France. The mission was a complete success. However, the batteries ran out quickly and the station stopped transmitting signals a few months after launch. Thirty-six stations of this type were built, fourteen of them deployed in the Arctic and sub-Arctic regions. As for U-537, it was sunk by an American submarine near the Dutch Indies (Indonesia) eleven months after the KURT mission; the crew was lost in the water. Only the two technicians and one crew member who stayed in Lorient provided information about this secret mission.

No one discovered the German weather station until 1977, when geomorphologist Peter Johnson, on a scientific mission in the region, came across the instruments and batteries he thought belonged to the Canadian government. Thanks to the work of a retired Siemens engineer, Franz Selinger, who was interested in his company's history, documents and photographs were found. KURT station equipment was placed on display at the War Museum in Ottawa in 1981.

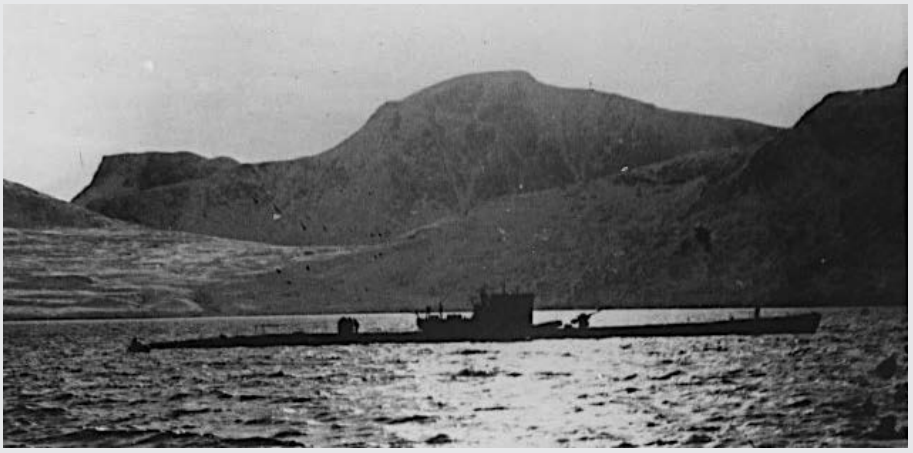


FIGURE 4.21: German submarine U-537 type IXC/40 in Martin Bay, Labrador, Newfoundland (now Canada) on October 22, 1943. On the ship's deck, sailors unload the components of the *Kurt* weather station onto rubber canoes. Source: Bundesarchiv, Germany.

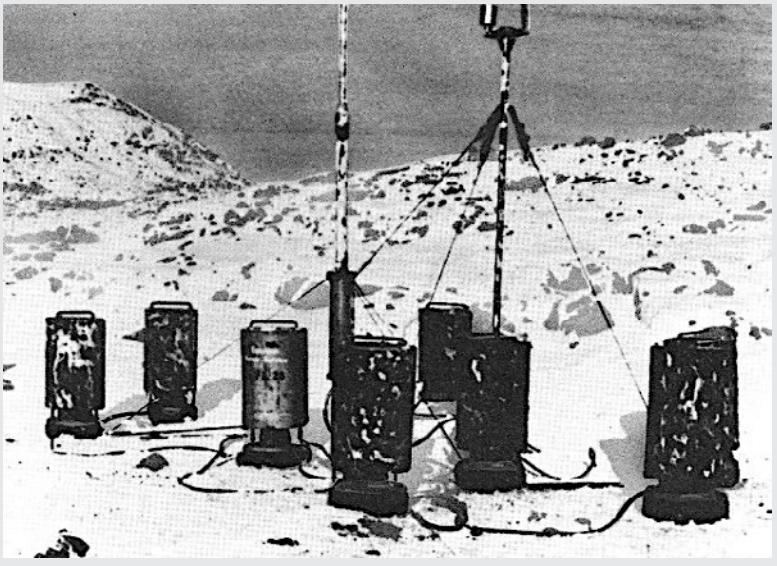


FIGURE 4.22: German weather station *Kurt* installed on the Hutton Labrador Peninsula, Newfoundland, October 22, 1943. Source: Bundesarchiv, Germany.

Box 4.4. Weather Forecasts for D-Day

The invasion of Normandy by American, British, Canadian and Australian allied forces was prepared in the early months of 1944. Equipment, including ships and landing craft, was being assembled along the English coast. Soldiers were undergoing intense training. Plans were taking shape. The planned date for the operation, called Operation *Overlord*, remained a secret, and only a few officers knew that it was set for June 5, weather permitting. The final decision had to be made by the Supreme Commander, General Dwight Eisenhower.

In early June, the weather in southern England deteriorated to an extraordinary degree as a series of cyclones formed in the North Atlantic and moved in sequence toward the British Isles and northern France. Third Reich meteorologists were reassured that the weather would be so bad that an invasion would be unlikely in the early days of June. German warships remained in port and aircraft were grounded. Some officers stationed along the Atlantic Wall were allowed to take a few days' leave.

On the Allied side, weather forecasting was entrusted to three groups of two forecasters, each working independently: the American group, consisting of Lieutenant Colonel Irving Krick and Lieutenant Colonel Ben Holzman (at the U.S. base at Widewing, 20 km west of London) and two British groups, one belonging to the British Meteorological Service (at Dunstable, 55 km north of London, with Douglas and Petterssen) and the other to the Royal Navy Weather Service (based at the Admiralty in central London, with Commander Wolfe and Lieutenant Hoggen). The three centers were connected by a simple telephone line, and the coordination of the forecasts was entrusted to James M. Stagg, a specialist in terrestrial magnetism; Stagg was also responsible for informing Eisenhower's Supreme Headquarters of the weather situation.

The Americans based their forecasts on a technique advocated by Krick and known as the *analogy technique*, which compares the current atmospheric situation with those that have occurred in a similar way in the past. The British, on the other hand, preferred to use a more traditional method known as short-range forecasting. On June 3, the Americans and British came to different conclusions, although they all expected the weather to worsen during the night of June 4-5. For the Americans, however, the invasion was considered "possible" by the morning of June 5, especially since the weather was expected to remain bad for the next few weeks. Failure to carry out the invasion could therefore delay the operation for several weeks. On the British side, on the other hand, it was clear that the storm would be violent enough to delay the great invasion of Europe. One had to wait for more favorable conditions. At the last moment, Stagg persuaded General Eisenhower to delay the offensive.

Just when the meteorologists seemed to be in disagreement, an important piece of information came from Ireland. On June 3, a young woman named Maureen Flavin (1923-2023), who was celebrating her 21st birthday that day, oversaw the weather observations that were taken every hour of the day and

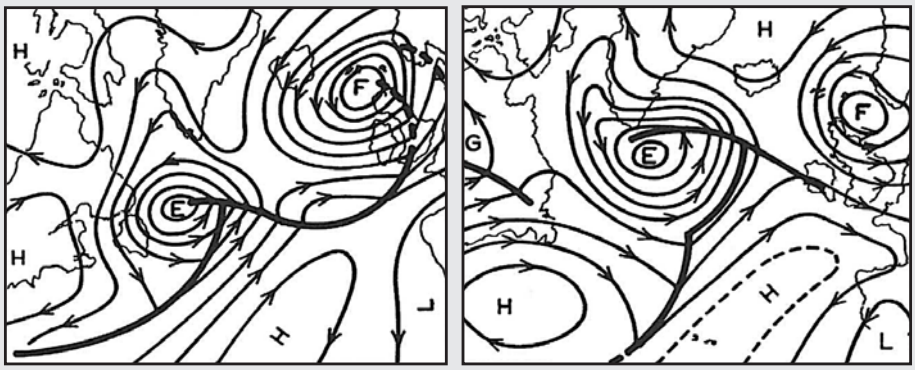


FIGURE 4.23: Weather situation on June 4, 1944 at 13:00 GMT (left) and June 6, 1944 at 6:00 GMT (right). Note the presence of low-pressure system F, which produced very strong winds in the English Channel and England on June 4. It slowly moved away from the region, and the winds in the Channel became less intense. The next low-pressure cell, E, moved toward Greenland, sparing the battle zone on June 6.

night and sent from the post office in the village of Blacksod in County Mayo, a peninsula in northwestern Ireland. It is an ideal place to "see" storms coming. At 1 a.m., M. Flavin noticed that the barometric pressure was dropping considerably; a strong low-pressure system was approaching Ireland and moving toward the British Isles and continental Europe. She called the Met Office in Dublin, which relayed the information to Allied Headquarters in England. A few hours later, on the morning of June 3, she received a call, presumably from London: a woman's voice urging her to check her readings: "Please check. Please repeat." Maureen called Edward "Ted" Sweeney (her future husband) who replied: "Yes, the barometer is dropping fast and a storm is coming". Eisenhower was informed. The landing date was postponed. Maureen Flavin's observations may have saved thousands of lives. The postwoman from Blacksod would learn ten years later that it was her message, sent in the middle of the night of June 3, that delayed the landing date.



FIGURE 4.24: Maureen Flavin.

Meanwhile, British and American meteorologists continued to monitor the weather. Sverre Petterssen (1898-1974), a talented meteorologist trained at the Norwegian School in Bergen, played an important role. This specialist in the upper atmosphere, who had been head of the meteorology department at MIT before joining the British Met Office to support the war effort, noticed that the upper wind trajectory was beginning to undulate, which should slow the progress of the cyclonic areas eastward. The next storm appeared to be moving slowly toward England. The various partners were convinced that this

was indeed the case and thus regained the spirit of consensus that no longer existed among the three groups of forecasters. They therefore instructed the military command that a brief improvement should occur on June 6, before the arrival of the next disturbance. General Eisenhower gave the signal for the troops to cross the Channel.

The difficulties encountered by meteorologists during World War II, and in particular the need for accurate weather forecasts for the armed forces, led several countries, especially the United States, to develop postwar atmospheric science research programs and new technologies essential to improving the quality of observations.

The Role of Electronic Computers

It wasn't until the development of electronic computers during and after World War II that significant progress was made in the development of atmospheric circulation models. The story begins in the historic town of Princeton, New Jersey, halfway between New York and Philadelphia. The town is famous for having fought a decisive battle during the American War of Independence (1775-1783) and becoming the temporary capital of the country for a few months. After the victory of the troops led by George Washington (1732-1799) and the retreat of the British soldiers to the south of the state, the Treaty of Paris of 1783 ended the war, and the British recognized the sovereignty of the United States of America. George Washington became the first President of the United States.

In the early 1930s, with the help of philanthropists Louis Bamberger (1855-1944) and Caroline "Carrie" Bamberger Fuld (1864-1944), Abraham Flexner[158] (1886-1959), a supporter of basic research, founded the Institute for Advanced Study[159] (IAS) in Princeton, where a prestigious university had already been established. The latter institution attracted eminent figures such as the physicist Albert Einstein (1879-1955), the mathematician John von Neumann (1903-1957), and the computer scientist Alan Turing[160](1912-1954). Before returning to his homeland to help decode German messages during World War II, Turing used his stay at Princeton to think about what a universal computer might be. Like von Neumann, he wanted to develop numerical methods for solving hydrodynamic

[158] In an essay entitled "The Usefulness of Useless Knowledge," Abraham Flexner defends the search for profound knowledge motivated solely by curiosity and without concern for applications.

[159] The *Institute for Advanced Studies* is an independent institution based in Princeton, but with no institutional ties to Princeton University. Its research programs are not subject to external funding constraints, and the scientists who are members of the institute have complete freedom to choose the subjects they wish to address. The institute has welcomed a number of top European researchers who decided to flee their Nazi-stricken homeland.

[160] Alan Turing succeeded in "breaking the *Enigma* code" used by the Nazis during the Second World War to transmit top-secret information, enabling the British services and their allies to learn about the intentions of the German military.

equations, such as those describing the motions of air in the atmosphere. He was convinced that this could only be achieved with a powerful electronic computer. The engineers responsible for developing nuclear weapons as part of the Manhattan Project felt the same need. So, it was the US Energy Commission and the military agencies that released the first funds to finance such initiatives.



AY, JUNE 7, 1930—10 PAGES TWO CENTS

Louis Bamberger and Mrs. Fuld Give $5,000,000 to Establish Institute of Advanced Learning

Donors of Institute Fund

Initial Endowment Announced For Graduate Foundation In Newark or Vicinity

The gift of $5,000,000 by Louis Bamberger and his sister, Mrs. Felix Fuld, to establish an educational foundation to be called the Institute for Advanced Study was announced today. It will be located "in Newark or its vicinity."

FIGURE 4.25: Louis Bamberger (1855-1944) and his sister Caroline Bamberger Fuld (1864-1944) announce that they are offering $5 million to establish what will become the Institute for Advanced Study in Princeton. Bamberger, of German descent, sold his department store to Macy's in 1928.

Meanwhile, in Pennsylvania, John William Mauchy (1907-1980), a scientist interested in the relationship between solar activity and weather conditions, was also calling for the construction of a supercomputer to analyze the vast scientific data available to him. In 1942, he joined the Moore School of Electrical Engineering at the University of Pennsylvania in Philadelphia, where he worked with the U.S. Army on calculating ballistic trajectories as part of the war effort. Mauchy received funding from the Army to build *the Electronic Numerical Integrator and Computer* (ENIAC) with his colleagues at the engineering school, in particular John Adam Presper Eckert (1919-1995).

It was a unexpected meeting on a train platform that brought von Neumann into contact with the ENIAC team. A professional relationship was established, and after the end of hostilities, the military's needed to calculate ballistic trajectories gave way to other priorities of national interest: the development of nuclear weapons and the need of reliable weather forecasts for military aviation.

In addition to the first computers, such as *Colossus*, developed in England in 1943 by mathematician Max Newman (1897-1984) with the help of Alan Turing and used by the military in 1944 to support the war effort, the first general-purpose computer was built at the University of Pennsylvania in Philadelphia between 1943 and 1945. ENIAC was a huge machine, 30 meters long, weighing 32 tons, with 18,000 electronic tubes and a power consumption of 150 kW. This digital computer was little known to the general public because it was protected by military secrecy. Programming was done by cables that were customized for each problem. In 1947, the machine was transferred to a U.S. Army facility, *Aberdeen Proving Ground*, in Maryland, where it remained in operation until October 1955.



FIGURE 4.26: János Lajos Neumann or John von Neumann.

János Lajos Neumann, or John von Neumann, born in Budapest, Hungary, is one of the most prodigious mathematicians mankind has ever known. He is often called the "father of supercomputing". He began his scientific career in Europe (Zurich, Berlin, Göttingen, Hamburg), focusing on pure mathematics and game theory. He also developed a rigorous mathematical formulation of quantum mechanics. From 1930, he taught regularly at Princeton University before joining the Institute for Advanced Studies three years later, with which he remained associated for many years. As a member of a Jewish family living in Eastern Europe, he decided to flee Nazism and emigrate to the United States. Beginning in 1943, he worked at the Los Alamos National Laboratory in New Mexico, contributing to the Manhattan Project. ENIAC offered unprecedented capabilities for performing the calculations needed to develop the hydrogen bomb. He therefore worked closely with the group of programmers at the computing center. After his time at Los Alamos, he devoted himself almost exclusively to applied mathematics and, aware of the dangers of the emerging Cold War, contributed to the defense efforts of his host country.

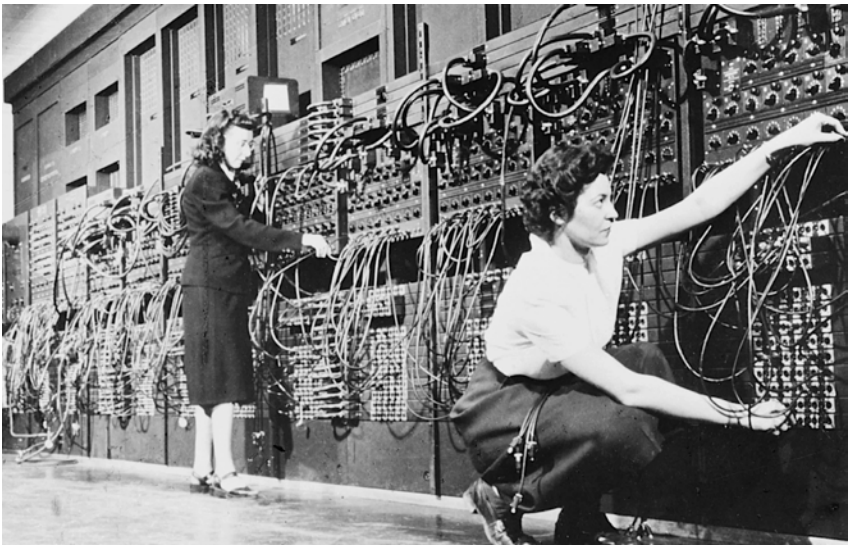


FIGURE 4.27: ENIAC, one of the first computers, developed by the University of Pennsylvania. This 2.5-meter-high, 30.5-meter-long, 30-ton computer performs 5,000 additions or 300 multiplications per second. Pictured are two of the machine's first programmers, Marlyn Wescoff (left) and Ruth Lichterman (right). Source: U.S. National Archives Education Updates.



FIGURE 4.28: Several leading scientists using ENIAC to develop a model of the atmospheric general circulation at the *Institute for Advanced Study* in Princeton. Pictured from left to right are Harry Wexler, John von Neumann, M. H. Frankel, Jerome Namias, John Freeman, Ragnar Fjörtoft, Francis Reichelderfer, and Jule Charney. Source MIT Museum.

On January 9, 1946, John von Neumann and Russian-born engineer Vladimir Kosma Zworykin (1888-1982), a pioneer in television technology who had become an associate director of the Radio Corporation of America, met in Washington to launch a revolutionary project: to develop a new electronic computer capable of solving the mysteries of long-range weather forecasting. As reported in the *New York Times*[161]:

> "If the super-calculator could be built and operated successfully, weather experts said, it not only might lift the veil from previously undisclosed mysteries connected with the science of weather forecasting but might even make it possible to "do something about the weather" through advanced application of scientific knowledge concerning countermeasures to unfavorable weather. The benefits to agriculture, shipping, air travel and other activities through advance knowledge of the weather were obvious, they added, and the savings in crops, money and even lives would be incalculable."

> And the newspaper added:

> "Mark Twain once observed that everyone talks about the weather, but no one does anything about it. This no longer is exactly true, as there have been successful though small-scale experiments in combatting such conditions as frost and fog. Now, scientists ask why it should not be possible to head off such disasters as typhoons, hurricanes and violent rainstorms if there is

[161] Shallet, S., Weather Forecasting by Calculator Run by Electronics is predicted, *The New York Times* (11 January 1945), 12 p., 1946.

knowledge sufficiently in advance where and when they will strike. Some scientists even wonder whether the new discovery of atomic energy might provide a means of diverting, by its explosive force, a hurricane before it could strike a populated place."

This paved the way for *the Electronic Discrete Variable Automatic Computer* (EDVAC), whose architecture von Neumann designed. He won the support of the meteorological community at a "Conference on Meteorology" he organized in Princeton on August 29 and 30, 1946.

The Development of Numerical Forecasting in the United States

The war effort highlighted the importance of weather forecasting, which was of interest to both academia and the military. At the same time, the development of the first computers brought a new hope: the ability to solve the equations of fluid mechanics numerically for operational purposes and to transform meteorology into a truly quantitative science. Several outstanding individuals, most of whom worked directly with von Neumann, were to play a major role. These included Carl-Gustaf Rossby at the Universities of Stockholm and Chicago, as well as Jule Gregory Charney (1917-1981) and Norman A. Phillips (1923-2019), both at the University of Chicago, the Institute for Advanced Study in Princeton, and the Massachusetts Institute of Technology (MIT) in Cambridge, near Boston. To this list should be added Bernhard Haurwitz (1905-1986), Philip Ducan Thompson (1922-1994), Joseph "Jo" Smagorinsky (1924-2005), George P. Cressman (1919-2008), and Frederick (Fred) Gale Shuman (1919-2005). The latter three were members of the National Weather Service. This group of scientists revolutionized the methods of weather forecasting.

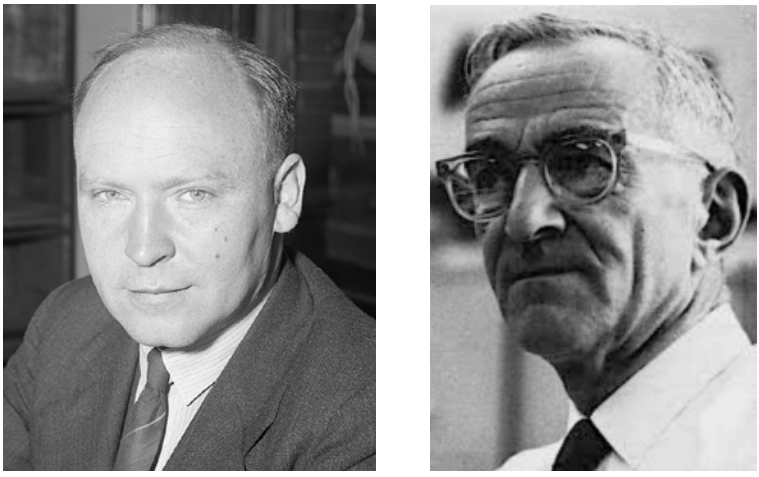


FIGURE 4.29: Carl-Gustaf Rossby and Bernhard Haurwitz. Source: NCAR.

In 1946, with the construction of the EDVAC running behind schedule, von Neumann suggested using the ENIAC to implement a program on atmospheric dynamics. The machine was particularly well suited to problems in this area. The time had come to repeat Richardson's work, but this time with new computing resources. John von Neumann approached Jule Gregory Charney (1917-1981), who had just completed his doctoral thesis on the propagation of waves in the atmosphere at the University of California, Los Angeles (UCLA). Charney joined the IAS in 1948. The mathematician and the meteorologist decided to join forces to develop a model that would enable rigorous weather forecasting.

The Barotropic Model. The formulation adopted for this model was based on two simplifying assumptions: first, the atmosphere was assumed to be an incompressible fluid and second, atmospheric motions were assumed to be purely horizontal. In this approach, wind is invariant with altitude, and temperature is constant over an isobaric surface (a surface of equal pressure). By making these choices, Charney greatly simplified the Bjerknes equations[162] and thus avoided the numerical problems encountered by Richardson. In fact, the system is reduced to a single equation, the Rossby[163] vortex equation. This model, known as the *barotropic model*, provides forecasters with a representation of large-scale air motion in the mid-troposphere. The numerical integration[164] of the equation was carried out by Charney and von Neumann at ENIAC in collaboration with the Norwegian meteorologist Ragnar Fjörtoft (1913-1998). The model successfully reproduced the actual meteorological situation. Despite the limitations inherent in the barotropic approach, the model was gradually improved and used for operational purposes by the American Weather Service until 1962. Models of this type were also developed in Sweden under the impetus of Gustaf Rossby and Bert Bolin (1925-2007). Bolin, a student of Rossby's at Stockholm University, worked with Charney and von Neumann at Princeton, where he participated in the development of atmospheric models. A similar effort was underway at the British Meteorological Office in Reading, England.

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[162] Charney adopted the hydrostatic approximation and the quasi-geostrophic approximation. This configuration eliminates fast-propagating but insignificant acoustic and gravity waves, but reproduces planetary waves and mesoscale meteorological disturbances. More recent high-spatial-resolution models no longer adopt these approximations.

[163] The vortex is proportional to the vertical component of the rotational wind speed.

[164] Charney, J.G., Fjörtoft, R., von Neumann, J., Numerical integration of the barotropic vorticity equation. *Tellus, 2*(4), 237-254, 1950. In the acknowledgements at the end of the article, we read: "The writers wish to thank Mrs K. von Neumann for instruction in the technique of coding for the ENIAC and for checking the final code, Professor G. Platzman of the University of Chicago for his considerable help and advice in coding the computations for the ENIAC, Mr J. Fremann of the Meteorological Research Group at the Institute for Advanced Study and Mr J. Smagorinsky of the U. S. Weather Bureau for their assistance in the preliminary work of data preparation and in the actual running of the computations on the ENIAC at Aberdeen." Professor Platzman also participated in the work at Aberdeen, where again his advice proved most valuable. We are also greatly obliged to the staff of the Computing Laboratory of the Ballistic Research Laboratories for help in coding the problem for the ENIAC and for running the computations.

The Baroclinic Model. In the 1950s, some critics argued that the barotropic model was too simple. It's true that it was mainly the limited computing power of ENIAC that led to the adoption of this type of model. The idea of developing a model with several superimposed atmospheric layers was gaining ground and interested the Weather Bureau, which sent several staff members to Princeton, in particular George Cressman, Frederick Shuman, and Joseph Smogorinsky. Smogorinsky would play a key role in the development of meteorological and climate research in the United States.

Smogorinsky, who spent his childhood in New York with a family of refugees from Belarus, was a passionate meteorologist. He joined the U.S. Air Force when the United States decided to enter World War II. Later, when he joined the U.S. Weather Bureau, he became an assistant to a very influential figure: Harry Wexler (1911-1962), head of the Special Scientific Services Division. At the instigation of Wexler, who knew the Princeton group well, Smagorinsky joined the IAS, initially as a programmer, which gave him the opportunity to prepare a Ph.D. thesis, which he defended at Princeton University. In the years that followed, this visionary scientist built a veritable center for meteorological and climate research at Princeton.

While waiting for the powerful computer they need to carry out their new projects, the team assembled at the IAS continued to explore the challenges of developing the capabilities of multilayer atmospheric models, known as *baroclinic models*. These are based on more complete equations describing hydrodynamic and thermodynamic processes. The development of such models is a real challenge due to the complexity of the processes involved. Moreover, the appearance of instabilities related to the numerical resolution of the equations can be a real difficulty, as was the case in Richardson's attempt. Norman Philips (1923-2019) oversaw the project. The first model, called the Princeton model and developed by Charney and Phillips, consisted of three atmospheric layers. A variant of this model became the operational forecast system used by the National Weather Service.

The scale of the task required new forms of collaboration, access to a powerful computer, and consequently increased funding. The project was of interest to the military, whose Air Force and Navy have a constant need for reliable weather forecasts for their naval aviation operations. In 1954, the Weather Bureau joined forces with the U.S. Air Force and Navy to form a consortium called the *Joint Numerical Weather Prediction Unit* (JNWPU). The goal of this partnership was to predict the three-dimensional distribution of atmospheric variables on a daily basis, thereby enhancing the capabilities of the participating weather services.

Several steps were envisioned. A first step was proposed in the late 1950s by JNWPU director George Cressman: the development of a multilayer model based on the *quasi-geostrophic approximation*. This approximation is based on a simplifying assumption: the quasi-equilibrium that exists between the force resulting from the horizontal pressure gradient and the apparent Coriolis force (due to the Earth's rotation) (see Box 4.2). Such a model has the advantage of not generating gravity waves, which could lead to numerical instabilities during the simulation. However, since the geostrophic equilibrium holds only outside the tropical zones, the model cannot be extended to the entire planet. Therefore, in the 1960s it was decided to implement a multi-layer model, this time based on the so-called *primitive* equations, i.e. those used by Richardson in his attempt

to make his first numerical prediction. The successor to the quasi-geostrophic model was a six-layer model. The principal architect of this project was Frederick Shuman, a meteorologist who had served in North Africa and Italy during World War II before earning his Ph.D. at MIT and joining the American Weather Bureau and the Advanced Study Program group at Princeton. One of the most delicate tasks for the authors of the new models was to choose initial conditions close enough to equilibrium to avoid numerical instabilities. The representation of the physical processes, in particular the components of the hydrological cycle (cloud formation, precipitation, etc.) was another challenge to be addressed.

The acquisition of a powerful computer to perform atmospheric simulations was a priority for the JNWPU. An IBM 701 series was chosen. This first-generation machine, based on the use of vacuum tubes like ENIAC, was the first computer produced by IBM for scientific and technical purposes, although several were acquired by the military. The architecture was largely based on that proposed by von Neumann.

Thanks to the work of these pioneers and the development of electronic computers, significant progress was made in the years that followed. In 1955, Jule Charney proposed that the Weather Bureau establish a permanent laboratory dedicated to modeling the atmospheric general circulation. The new group was established in Washington, DC, under the leadership of Joseph Smagorinsky.

Charney left Princeton in 1956 to join MIT. Like von Neumann, he was interested in the future of the planet in general and wondered about the benefits that might be derived from climate manipulation. But he remained cautious, adding that what *can* be done is no justification for what *must* be done. Von Neumann died at the age of 53 of cancer, possibly caused by the effects of the radiation he had been exposed to at Los Alamos. On his deathbed, he is said to have recited several passages from Goethe's *Faust* to his brother. He converted to Catholicism in 1930 and is said to have often taken up the philosophical arguments of Blaise Pascal:

> "So long as there is the possibility of eternal damnation for nonbelievers it is more logical to be a believer at the end."

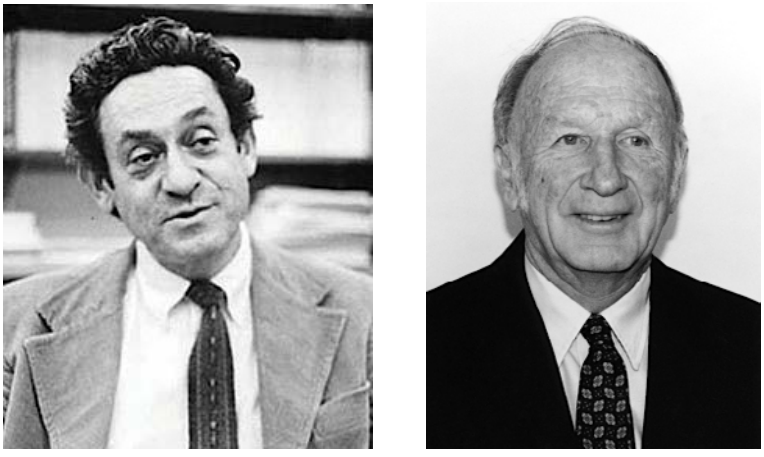


FIGURE 4.30: Two pioneers of modern meteorology at MIT: Jule Charney (left) and Ed Lorenz (right).

In 1963, the Weather Bureau laboratory was renamed the *Geophysical Fluid Dynamics Laboratory* (GFDL), and today it is an integral part of NOAA, the U.S. National Oceanic and Atmospheric Administration, which was created in 1970. However, Smagorinsky wanted to bring GFDL closer to a prestigious university and decided to move its operations from Washington to Princeton.

In the mathematical models mentioned above, the Earth is surrounded by a fictitious grid, and an approximate solution to the equations of atmospheric dynamics is sought for each point on the grid[165]. In many cases, the grid is made up of meridians and geographic parallels, but other types of grids have been used to avoid the appearance of numerical problems near the poles, i.e., in the region where the meridians converge to a singular point. Bernhard Haurwitz, a German meteorologist working in the United States, proposed a method of solving the equations that takes into account the sphericity of the Earth and does not require the use of a numerical grid. Haurwitz played a leading role in the development of atmospheric science during World War II and the years that followed.

After receiving his doctorate and habilitation from the prestigious University of Leipzig in Germany (1927 and 1931), Bernhard Haurwitz traveled to the United States in 1932, where he took a temporary position at MIT and worked with Carl-Gustaf Rossby. While visiting the California Institute of Technology (Caltech) in Pasadena, California, he learned that Hitler had become Chancellor of the German Reich and decided not to return to his homeland. He remained in America, working first in Canada and then, in 1941, returning to MIT (at the invitation of Sverre Petterssen) before joining New York University, where he spent most of his career as a professor. A member of the U.S. Academy of Sciences and Germany's prestigious Leopoldina Academy of Natural Scientists, he spent several years teaching geophysics at the National Center for Atmospheric Research (NCAR) and the Universities of Boulder and Fort Collins in Colorado. He also made numerous visits to the Geophysical Institute in Fairbanks, Alaska, where he worked on upper atmosphere problems.

As early as 1939, Haurwitz turned his attention to the conceptual model developed by Carl-Gustav Rossby. This model makes it possible to find simple solutions to the vortex equation. It represents the atmospheric circulation on a plane subject to a rotation with a period equal to that of the Earth's rotation. In 1940, Haurwitz generalized this method to a spherical geometry, paving the way for the first weather forecasting models to be developed ten years later. He proposed to express atmospheric variables in terms of a finite series of spherical harmonic functions (i.e., the superposition of planetary waves of different sizes). This elegant approach, which is the basis of the so-called *spectral models*[166], was conceived in 1970 by MIT mathematician Steven Alan Orszag (1943-2011)

[165] In this method, partial derivatives along spatial directions are replaced by finite differences calculated at each grid point. The distance between grid points characterizes the spatial resolution of the model.

[166] Orszag, S.A., Transform method for calculation of vector-coupled sums: Application to the spectral form of the vorticity equation. *Journal of the Atmospheric Sciences 27,* 890-895, 1970.

and has been used successfully for decades[167]. It was introduced for operational weather forecasting in most countries in the 1970s and 1980s. Today, it is gradually being abandoned in favor of older grid-point methods that are better suited to modern computers based on parallel computing architectures.

In summary, modeling efforts in the United States since World War II have led to significant advances in weather forecasting. Since the 1950s, efforts have focused on reducing the simplifications that characterized early models and on gradually increasing the spatial resolution used to represent the physical and dynamic processes of the atmosphere. These developments were directly related to the increase in available computing power. Initially, most models were based on the finite difference technique, computed on a numerical grid covering the planetary sphere. Since the 1970s, other techniques have been introduced, notably the spectral method. Modeling efforts have been strongly inspired by the concept of causal determinism proposed by Laplace in 1814 and applied to meteorology by Bjerknes in 1904. However, a fundamental question arises: is the atmospheric system described by the fundamental equations of hydrodynamics and thermodynamics really a deterministic system? And if so, why can't we correctly predict the evolution of the atmosphere beyond a few days?

Atmosphere and Chaos

At the beginning of the twentieth century, astronomers were asked a similar question: was the solar system as stable as Pierre-Simon de Laplace claimed? Not so for the French mathematician, physicist, and philosopher Henri Poincaré[168] (1854-1912), whose work focused on the differential equations used to describe planetary motion and, in particular, to solve the famous three-body problem[169]. Poincaré entered a competition sponsored by King Oscar II of Sweden on the stability of the solar system and won the prize in 1889. Initially, he showed that

[167] Born in Manhattan, Steven Orszag graduated from MIT with a degree in mathematics at the age of 19. He continued his studies at Cambridge University in the United Kingdom and at Princeton University, where he earned a Ph.D. in astrophysics. This brilliant mathematician became a professor at MIT in 1967, then at Princeton University in 1984, and finally at Yale University in 2000. His work focuses on fluid mechanics, particularly spectral methods and the treatment of equations applied to turbulence.

[168] Ruelle, D., *Henri Poincaré, Science et Méthode*, Chapter V., Le Hasard, Flammarion, 1908.

[169] In 1885, the journal *Acta Mathematica*, edited by Gösta Mittag-Leffler (1846-1927), announced a prize to reward the person who could solve the famous N-body problem. The goal was to solve the differential equations representing the trajectories of mutually attracting material points according to Newton's law. Poincaré submitted his thesis on the 3-body problem on May 17, 1888, and was awarded the prize (2,500 Swedish crowns) by King Oscar II on January 21, 1889. The young Swedish mathematician Lars Edvard Phragmén (1863-1937), who oversaw preparing the publication of the memoirs, asked Poincaré to clarify certain passages in the text. This led Poincaré to discover an "important error" in his work and to modify the text of his memoirs considerably. In January 1890, the French mathematician submitted a new 270-page version to replace the prize-winning 158-page dissertation. He paid the printing costs of the

the orbits of the planets were indeed stable, as Laplace had suggested, but in writing the dissertation summarizing his research, he discovered an error in his preliminary work (for which he had been awarded the prize) and showed that celestial dynamics was chaotic and therefore not predictable in the long term. In other words, the trajectory of the planets, as determined by solving the differential equations, is highly dependent on the initial conditions used for the calculation. With this discovery, Poincaré introduced the concept of *deterministic chaos*, laying the foundation for modern chaos theory. Once again, work in astronomy was helping to advance meteorology and other sciences. In fact, we now know that atmospheric motions are chaotic, which means that the evolution of an atmospheric situation is highly dependent on the value of the initial conditions. Since the latter are imperfectly known, this poses a difficulty when trying to predict weather conditions. On this subject, Poincaré wrote in his book *Science et méthode*:



FIGURE 4.31: The French mathematician Henri Poincaré.

> "Why do meteorologists find it so difficult to predict the weather with any certainty? We see that major disturbances generally occur in regions where the atmosphere is in an unstable equilibrium. Meteorologists can see that this equilibrium is unstable, that a cyclone will be formed, but where? They can't say. A tenth of a degree more or less at any point, the cyclone bursts here and not there, and spreads its devastation over regions it would otherwise have spared. If they had been aware of this tenth of a degree, they could have predicted it in advance. But observations weren't close enough or precise enough, and this is why everything seems to be due to the intervention of chance. Here again, we find the same contrast between a tiny cause, inappreciable to the observer, and considerable effects that are sometimes appalling disasters."

This view was shared by meteorologist Edward Norton Lorenz (1917-2008), who studied the evolution of weather systems at MIT. To carry out his work, the research team used a computer that performed 400 operations per second: the vacuum-tube Royal McBee LPG-30, whose computing power was similar to that of ENIAC, but which had 100 times more memory for programs and

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original dissertation, which were higher than the prize money. It was in the corrected version of the text published in the journal that Poincaré mentioned the possible existence of unstable orbits, i.e. chaotic behavior of the planetary system.

data. To study the evolution of atmospheric disturbances, Lorenz tried to solve a nonlinear system containing 12 equations corresponding to 12 initial values. The results obtained by the computer were surprising: they were characterized by a chaotic solution.

To further explore the properties of these nonlinear systems, Lorenz then turned to more conceptual questions with systems containing fewer variables. In the course of this work, he performed a curious experiment. He decided to repeat the numerical simulation he had just performed on his computer. The initial conditions used in both cases were identical, but with a slight difference that Lorenz didn't immediately notice; in the first case, he had specified these conditions with 6 significant figures, whereas in the second, he had retained only three. Lorenz found that the solutions obtained in the two runs of his program were very close during the first few days of the simulation. What surprised him, however, was that these solutions began to diverge during the second part of the calculation, and in fact, each evolved toward a completely different state. This chaotic system is called *deterministic* because its evolution is determined by the value of the initial conditions, as opposed to *stochastic* systems whose evolution is completely random and therefore unpredictable.

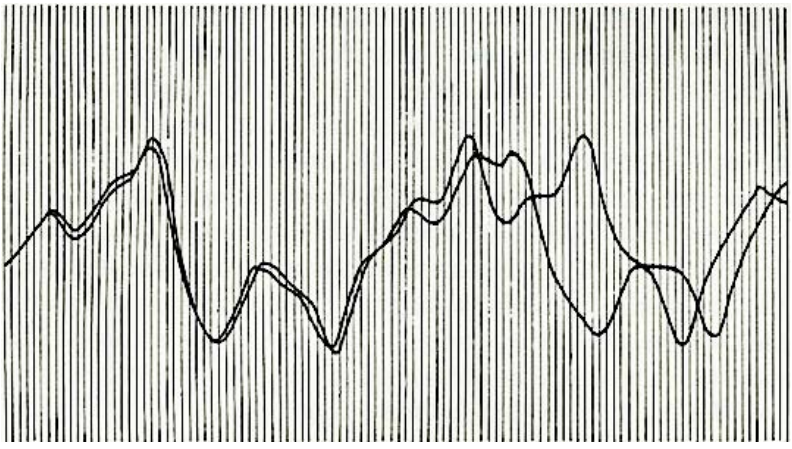


FIGURE 4.32: The difference between two weather forecasts started with very similar, but not identical, initial conditions. The two solutions are similar from the beginning of the integration but become more and more different as a function of time.

Two computer scientists, whose contribution has not been sufficiently emphasized, worked directly with Edward Lorenz. These "hidden heroes of chaos theory" are Margaret Elaine Hamilton and Ellen Cole Fetter Gille. Hamilton joined MIT's meteorology department in 1959, where she developed computer programs for weather forecasting and contributed directly to Lorenz's work. Later, in another MIT lab, she developed the on-board flight software that guided NASA's Apollo missions when American astronauts landed on the moon. As for Ellen Fetter, who succeeded Hamilton in the Lorenz group in 1961, she solved the equations describing convective motions, directly contributing to the development of chaos theory.




FIGURE 4.33: Left: Ellen Cole Fetter; right: Margaret Elaine Hamilton.

The implications of the discoveries made by Lorenz and his team at MIT are important for questions of weather forecasting and for the science of complex systems in general. In awarding the 1991 to Lorenz Kyoto Prize for Basic Science in Earth and Planetary Sciences, the judges commented on the discovery of *deterministic chaos*:

> "Lorenz's work has profoundly influenced a wide range of basic sciences, and has led to one of the most dramatic changes in humanity's view of nature since Sir Isaac Newton."

Since the initial values used in meteorological models are based on highly spatially inhomogeneous observations that contain uncertainties related to measurement errors, a deterministic forecast as envisioned by Bjerknes is possible only for a very limited period of time. Lorenz summarized his research in 1963[170]:

> "Two states differing by imperceptible quantities may eventually evolve into two considerably different states [...]. If, then, there is any error whatever in observing the present state - and in any real system such errors seem inevitable - an acceptable prediction of an instantaneous state in the distant future may well be impossible [...]. In view of the inevitable inaccuracy and incompleteness of weather observations, precise very-long-range forecasting would seem to be non-existent."

In 1969, he introduced an image that symbolizes his concept and shows symbolically how much the future evolution of the state of the atmosphere can depend on a signal that is imperceptible in the initial situation:

> "Can the flap of a butterfly's wings in Brazil trigger a tornado in Texas?"

However, Lorenz added an important element:

> "More generally, I propose the idea that [...] small disturbances neither increase nor decrease the frequency of climatic elements."

[170] Lorenz, E., Deterministic nonperiodic flow. *Journal of the Atmospheric Sciences*, 1963.

In other words, even if the evolution of a particular system is sensitive to initial conditions, the statistics that characterize the evolution of that system (e.g., mean values and variability) would be insensitive to those initial conditions. The statistics of the future, such as the mean state of tomorrow's climate, would therefore not depend on small, system-specific perturbations. As a result, all trajectories determined with slightly different initial conditions gradually approach the same point in phase space. This point is called the *attractor,* and the system is predictable despite its chaotic evolution.

To account for the random nature of atmospheric motions, weather forecasting today is based on a series of simulations performed with slightly different initial values, which in reality reflect the uncertainties in the meteorological observations used as starting conditions. Each forecast realization corresponds to a meteorological evolution trajectory in phase space, leading to a particular value of the calculated atmospheric quantities. From all these realizations, an average weather forecast is derived, expressed as the probability of a given event, such as the arrival of a precipitation area, occurring at a given location and time.

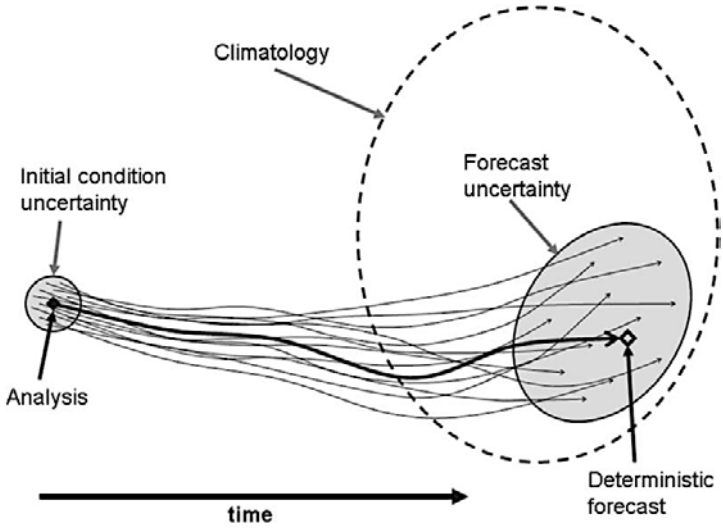


FIGURE 4.34: Representation of a probabilistic weather forecast. On the left, we show the initial conditions represented by a black diamond and the space of uncertainties surrounding this initial value. In the center, the trajectories showing the evolution of the atmospheric system over the time period corresponding to the forecast deadline. The bold line corresponds to the deterministic forecast made with the initial conditions deemed most probable (black diamond). The finer lines correspond to other realizations of the forecast obtained for different initial values, but contained within the space of uncertainties. On the right, the diamond represents the future meteorological situation obtained by the deterministic forecast. The grey area corresponds to the set of possible situations based on probabilistic forecasts, and shows the uncertainty associated with the forecast. Climatology (average situations over many years) is represented by the area surrounded by the dotted line. Probabilistic forecasting therefore offers real added value to climatology. It makes it possible to estimate the uncertainty of a weather forecast. Source: Windy Community on the Web.

The mathematician Etienne Ghys[171] sums up the evolution of thought brought about by Poincaré and Lorenz:

> "This new vision is much more useful than the Newtonian one, because it somehow allows a little individual freedom. The trajectories of the dynamic system have their own individuality, each following its own path. But even if these paths are very different from one another, they share a common statistic. This reconciles the idea of determinism, as Laplace understood it, with that of the probabilistic world."

Turbulence

Although the ancient Greek Aristotle distinguished between natural and violent air movements, it wasn't until the 16th century that Leonardo da Vinci systematically observed and described the irregular motions that disrupt a body of water under the influence of a jet of water. This was his first study of a chaotic phenomenon that remains largely mysterious. Centuries before the introduction of the mathematical foundations of hydrodynamics, da Vinci drew the eddies of water of various sizes that form and interact with each other before being damped and disappearing. Da Vinci wrote:

> "Observe the movement of the water's surface, which resembles that of hair, with two movements: one is caused by the weight of the hair, the other by the direction of the curls; thus the water possesses swirling movements, one part of which is due to the main current, the other to random, reverse movement."



FIGURE 4.35: Studies by Leonardo da Vinci (c.1510-12) of whirlpools in water under the effect of a water jet. Source: Royal Collection Trust Copyright Her Majesty Queen Elizabeth II 2021.

[171] Ghys, E., *La théorie du chaos*, CNRS Éditions, De Vive Voix, 57 pp., Paris, 2023.

The word turbulence, derived from the Latin *turbulentus* (agitated, disturbed), appears to have first appeared as *turbolenza* in the *Codex Atlanticus*, a collection of writings and drawings by Leonardo da Vinci. The name was quickly forgotten and did not reappear until 1887 in a text published by William Thomson (Lord Kelvin). Several eminent specialists in fluid mechanics, including the French mathematician and physicist Joseph Valentin Boussinesq (1842-1929), preferred to speak of "turbulent flow" and "vortex agitation". The Irish mathematician Osborne Reynolds (1842-1912) used the terms "sinuous motions" and "irregular vortices" to describe stochastic fluid flows. And it wasn't until 1917 that the Englishman Sir Geoffrey Ingram Taylor (1886-1975), who was working on turbulent exchange in air, adopted the name *turbulence*[172]. The German engineer Ludwig Prandtl (1875-1953), who introduced the concept of the *boundary layer* in flows, waited until 1921 to use the term.

Early studies of turbulence were essentially empirical or semiempirical. Reynolds, a graduate of Cambridge University and professor of engineering at the University of Manchester, was interested in the conditions under which turbulence occurs. In 1883, he published a famous paper in which he showed that the flow of a liquid in a pipe, which is regular at low velocity, takes on an irregular and chaotic form as the fluid velocity increases and exceeds a certain threshold.

Laminar conditions[173] correspond to a fluid composed of stable, stratified layers[174]. The transition to turbulent conditions occurs when the inertial forces, which tend to create instabilities in the fluid, become significantly greater than the viscous forces, which dampen vortex structures. The threshold for chaotic and unpredictable motion, i.e., the onset of turbulent flow, occurs when the *Reynolds Number*[175] generally exceeds a value close to two to three thousand.

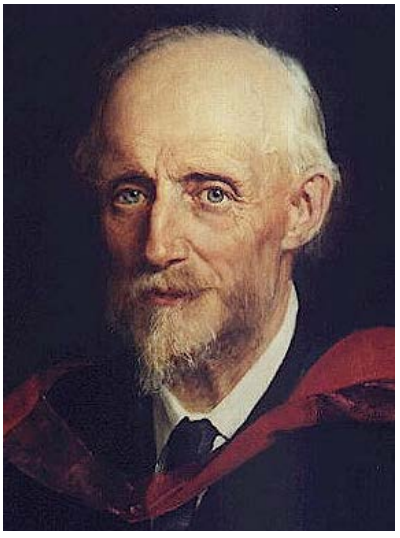


FIGURE 4.36: Osborne Reynolds.

Reynolds proposed to decompose the hydrodynamic quantities by the sum of two components: the mean value of these quantities (essentially representing regular motions) and a fluctuating component (representing turbulent motions). This decomposition of

[172] Taylor published in 1915 an article entitled "Eddy motions in the Atmosphere" (*Philos Trans. Roy. Soc. London A 215*, 1-26, 1915) and Prandtl in 1932 an article entitled "Meteorologische Anwendungen der Strömungslehre" (*Beitr. Phys. Fr. Atmosph. 19*, 188-202, 1932).

[173] From the Latin *laminae*, thin layer.

[174] With the less dense layers overhanging the denser ones.

[175] The "Reynolds number" is defined as the ratio between the forces of inertia and the forces of viscosity that apply to the fluid. This number reaches, for example, values between 10^9 and 10^{12} in the Earth's atmosphere.

the velocity, temperature, and density fields makes it possible to determine the correlations that exist between these different physical quantities and, in particular, the mass and energy flows generated by turbulence.

Among those who played a key role in fluid mechanics research was Graham I. Taylor (1886-1975). Taylor became interested in the mathematical formulation and physics of turbulence at Trinity College, Cambridge University, where he worked under the supervision of Sir Joseph John Thomson (1856-1940), known for his discovery of the electron and winner of the Nobel Prize in Physics (1906). Taylor used his time as a meteorologist on the icebreaker Scotia to study the mixing processes that occur in air under the influence of turbulent motion. With the outbreak of World War I, he applied his knowledge of hydrodynamics to the development of early aircraft. In 1944-1945, he was one of a group of British scientists who joined the secret Los Alamos Center in New Mexico to develop the atomic bomb. At the invitation of the center's director, General Leslie Groves (1886-1979), Taylor witnessed the first atomic test in the American desert.

Other scientists left their mark on the development of fluid dynamics. The Austro-Hungarian-born American physicist Theodore von Karman (1881-1963) made a major contribution to the advancement of aeronautics and astronautics in the first half of the twentieth century. This engineer is considered one of the leading theorists of aerodynamics. In fact, he developed a model of turbulence that was adopted by the U.S. Department of Defense for aeronautical studies. With the rise of Nazism in Europe, von Karman emigrated to the United States in 1930, where he became director of an aeronautics laboratory at the California Institute of Technology in Pasadena. In 1944, he founded the Jet Propulsion Laboratory, now part of NASA, and in 1956 the institute that bears his name in Rhode-Saint-Genèse, near Brussels.

Ludwig Prandtl (1875-1953), another brilliant figure in turbulence research, was interested in aerodynamics and also contributed to the development of aviation, but this time in Germany. This engineer, often considered the "founding father" of fluid dynamics, became famous for introducing the concept of the *boundary layer*[176]. In August 1904, he traveled to Heidelberg to attend the Third International Congress of Mathematicians. He was not yet well-known among his peers, and the time allotted for his talk on the subject was only ten minutes. But the work he was about to present would revolutionize fluid mechanics and would be essential for aeronautics in particular. It would also make it possible to describe the movement of air in the atmospheric layer near the Earth's surface. His work, which still serves as a reference today, was published in 1905 under the title *On Fluid Motion at Very Small Friction*[177].

[176] Thin layer of fluid in the immediate vicinity of a boundary surface formed by the fluid flowing along this surface. Fluid interaction with the wall induces a no-slip boundary condition (zero velocity at the wall).

[177] Prandtl, L., Über Flüssigkeitsbewegung bei sehr kleiner Reibung. *Verhandl III, Intern. Math. Kongr. Heidelberg 1984*, Auch: *Gesammelte Abhandlungen*, 2, 484-491, 1905.

From 1925 to 1946, Prandtl headed the Kaiser Wilhelm Institute for Fluid Dynamics in Göttingen, where he developed the theory of shock waves in supersonic flows. A supporter of the Nazi regime, he became chairman of the Luftwaffe Research Directorate and the Luftwaffe High Command in 1942. Prandtl wrote that "Fascism in Italy and National Socialism in Germany represent very good beginnings of new thinking for the economy". In correspondence with G. I. Taylor, he was quick to point out that "the struggle which Germany unfortunately had to fight against the Jews is necessary for its own preservation". In 1946, he resumed his directorship, this time at the Max Planck Institute for Fluid Dynamics, but resigned a few months later.

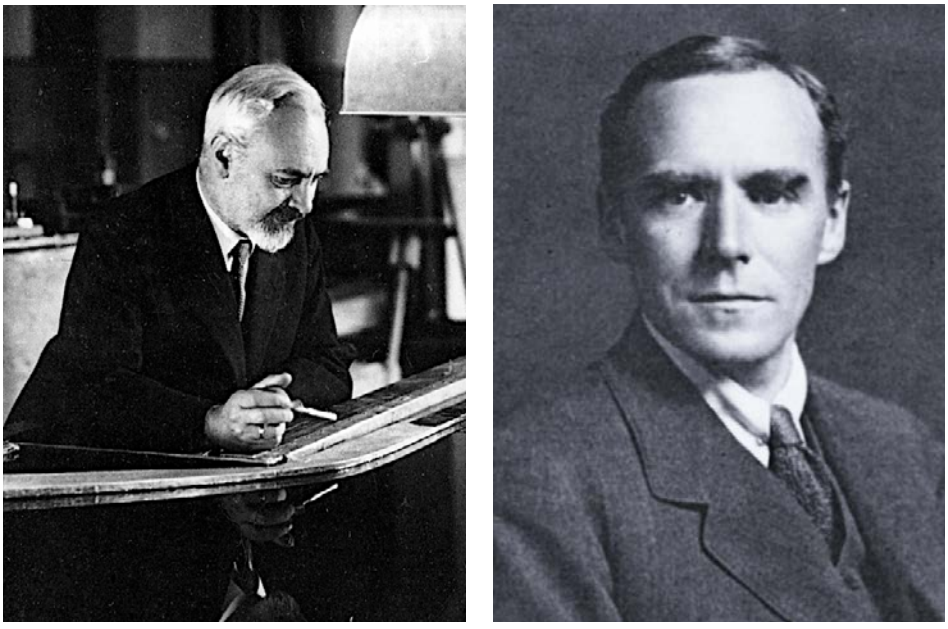


FIGURE 4.37: Left: Ludwig Prandtl in his laboratory in the mid-1930s. Reproduction from the original photograph DLR: FS-258. Right: Sir Geoffrey Ingram Taylor in 1919, copyright reserved.

Could meteorology benefit from these early studies of turbulence? The British meteorologist Lewis Fry Richardson (1881-1953) was convinced that it could. He believed that improved weather forecasting required a better understanding of the fundamental processes that determine the irregular air movements observed in the atmosphere. He therefore decided to follow the precise trajectory of a series of balloons launched in England and dispersed over Europe under the influence of turbulent air currents. He deduced that the vortices and spirals associated with turbulence behaved on a large scale like molecules in air and that the behavior of a fluid could therefore be described by analogy with concepts borrowed from molecular physics: viscosity and diffusion. However,

subsequent studies have shown that this comparison is unsatisfactory, not least because, unlike molecules, the dynamic structures within fluids are characterized by a variety of interacting spatial scales. For example, Richardson found that large eddies become unstable and break up into smaller ones. This process continues, forming a cascade that transfers energy from large motions to smaller structures. At the end of the chain, the smaller vortices dissipate under the effect of the fluid's viscosity. This concept is well summed up in the poem, which Richardson adapted from lines by the Anglo-Irish satirical poet Jonathan Swift (1667-1745):

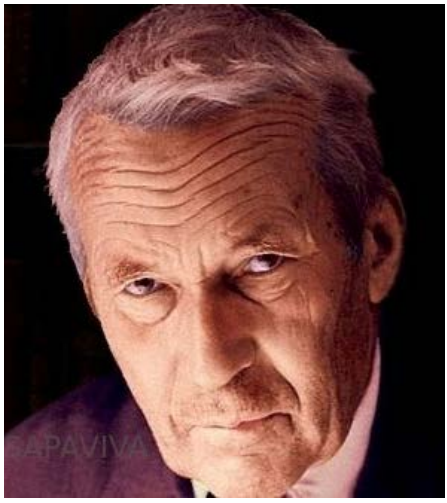


FIGURE 4.38: Andrey Kolmogorov, copyright reserved.

> "Big whirls have little whirls
> that feed on their velocity,
> and little whirls have lesser whirls
> and so on to viscosity"

In the Soviet Union, the mathematician and physicist Andrey Kolmogorov (1903-1987) used Richardson's ideas to establish statistical properties and develop a phenomenological theory applicable to isotropic and homogeneous turbulent flows. Based on several hypotheses, he theoretically determined the energy spectrum of turbulence and showed that the energy of vortex structures varies according to a power law of minus 5/3. This result, obtained in 1941 and subsequently confirmed by experiment, is applied to the study of the physical processes involved in various meteorological and oceanographic phenomena. Recent work has shown the limitations of this theory. In particular, small turbulent structures tend to dissipate, which is now represented by the notion of turbulent viscosity, a concept introduced in 1877 by the French mathematician Joseph Boussinesq (1842-1929).

Kolmogorov's work greatly influenced the study of turbulence. This talented scientist, who became interested in probability theory at an early age, spent long periods at the universities of Göttingen, Munich, and Paris before joining Moscow State University as a professor. In 1939, he was elected to the USSR Academy of Sciences. A few years earlier, during the *Great Purge* of 1936 in the Stalin-led Soviet Union, in which millions of people were arrested or executed, the Russian school of mathematics came under severe attack at a time of generational conflict. Kolmogorov and several of his colleagues testified against their former teacher and thesis supervisor, the Russian mathematician and one of the founders of the Russian school of mathematics, Nikolai Nikolaevich Luzin (1883-1950), accusing him of plagiarism, nepotism, and other shortcomings. As part

of the Sovietization of scientific research, Luzin was also criticized by the newspaper *La Pravda*[178] for publishing his articles in French instead of publising them in Soviet scientific journals. To convince Kolmogorov to testify against his former boss, the Soviet authorities threatened to reveal a homosexual relationship he had with the mathematician Pavel Sergeyevich Alexandrov (1896-1982), also a student and one of Luzin's main accusers. The 1936 verdict declared Luzin an "enemy of the people". He was dismissed from the university and his research institute was closed, but, contrary to expectations, he was neither arrested nor expelled from the USSR Academy of Sciences.

Other Russian scientists also contributed to the study of turbulence. Among them are Andrei Sergeevich S. Monin (1921-2007) and Alexander Mikhailovich Obukhov (1918-1989), two students of Kolmogorov. They developed a theory of similarity based on universal relations between nondimensional variables and applied it to the surface layer of the atmosphere. From 1943, Monin participated in the Red Army's war effort as a weather forecaster, and in 1946 he joined Kolmogorov's group at Moscow State University. He continued his career at the Institute of Geophysics of the USSR Academy of Sciences. Together with his colleague Akiva Moiseyevich Yaglom[179] (1921-2007), he published a book in 1965 that is now considered a classic work on turbulence theory[180]. As for Obukhov, he is considered one of the leading specialists in boundary layer meteorology. It was he who introduced the concept of the universal exchange length in the surface layer of the atmosphere, the basis for the theory of similarities now known as the Monin-Obukhov theory.

However, it wasn't until the early 1940s that the first mathematical formulations for dealing with turbulence were proposed. These were based on the Navier-Stokes equations. An important contribution, taking into account the concepts developed by Reynolds, was made by the Chinese scientist Zhou Peiyuan[181] (1902-1993). This scholar developed the equations describing the time evolution of the first-, second-, and third-order moments and proposed a closure relation for the system that allowed it to be solved in principle. Zhou, a former student at the University of Chicago and Caltech in Pasadena, then a postdoctoral fellow at the University of Leipzig with Werner Heisenberg and

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[178] The Pravda pamphlet ends cruelly for Luzin: "The Soviet scientific community is tearing off the mask of an honest scientist, leaving you completely in the shadows, and so you will appear to the world as a ridiculous individual who claims to defend 'pure science' but in reality betrays the interests of science and trades on it to appease your former bosses - the current masters of fascist science. The Soviet community will perceive the story of Academician Luzin as yet another object lesson in the fact that the enemy never lays down his arms, that he skillfully camouflages himself, that the methods of his mimicry are diversified, and that vigilance remains the most necessary effort of every Bolshevik and every Soviet citizen."

[179] Former student of Kolmogorov, Researcher at the Institute of Theoretical Geophysics (A. M. Obukhov Institute of Atmospheric Physics) then at the Massachusetts Institute for Technology (MIT) in the USA from 1992.

[180] "*Statistical Fluid Mechanics: Mechanics of Turbulence*", Volumes I and II, English translation, Dover Publications, 1971.

[181] *Chinese Journal of Physics*, *4*(*1*), 1-33, 1940.

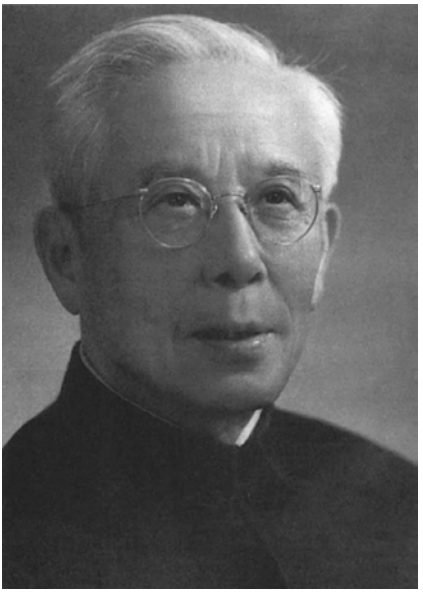


FIGURE 4.39: Zhou Peiyuan.

at the Polytechnic Institute of Zurich with Wolfgang Pauli, began his career at Tsinghua University in Beijing, working on problems in general relativity and gravity. With the outbreak of World War II, he changed his scientific orientation and devoted himself to the theoretical study of turbulence. He joined Peking University in 1952, first as a professor and then as its president in 1976. Zhou lived through some tragic times for China: the Japanese invasion, the war, the conflicts between Communists and Nationalists, and the Cultural Revolution. Although he opposed the *Gang of Four* who led the Cultural Revolution, he remained an ardent defender of basic research, which was considered a remnant of a bourgeois approach by the rulers of the time. However, he survived these troubled times and was even appointed to reform university teaching and research in 1976. More details about the development of atmospheric sciences in China are provided in Box 4.5.

At the time Zhou developed his formalism, computers were not yet available. Solving the equations was therefore difficult, partly because it could only be done by hand, and partly because the mathematical treatment of the equations was made particularly complex by the nonlinear interactions that characterize turbulent flows. The American physicist Richard Feynman (1918-1988) observed that turbulence remains the most important unsolved problem in classical physics. According to Harvard University Professor Sydney Goldstein[182] (1903-1989), the great English hydrodynamicist Horace Lamb[183] (1849-1934) said in 1932 at a meeting of the British Association:

> "I am an old man now, and when I die and go to Heaven there are two matters on which I hope for enlightenment. One is quantum electrodynamics, and the other is the turbulent motion of fluids. And about the former I am really rather optimistic."

However, two researchers, Steven Alan Orszag (1943-2011) and his colleague G. S. Patterson, struck a more optimistic note. During a several-month stay at the National Center for Atmospheric Research in Boulder, Colorado, they

[182] Goldstein, S., Fluid mechanics in the first half of this century. *Annual Review of Fluid Mechanics*, *1*, 1-29, 1969. In this article, British mathematician Goldstein, a Fellow of the Royal Society, quotes from memory Lamb's 1932 speech.

[183] Horace Lamb, British mathematician, professor at the Universities of Cambridge (1872-1875), Adelaide (1876-1885) and Manchester (1885-1920), member of the Royal Society and author of *Hydrodynamics*, published in 1895 by Cambridge University Press.

successfully numerically simulated a homogeneous, isotropic turbulent flow based on a spectral method[184]. In their paper[185] published in 1972, they wrote:

> "There has been much pessimism concerning the prospects for numerical simulation of three-dimensional turbulent flows. This pessimism seems well founded for the accurate numerical simulation of huge-Reynolds-number flows, but our results show that numerical simulation is feasible and even economical at Reynolds numbers like those achieved in wind-tunnel turbulence experiments."

This early work paved the way for a new discipline called "Computational Fluid Dynamics" with applications in industrial fields such as aeronautics as well as small-scale atmospheric dynamics. Today, three types of models based on the solution of the Navier-Stokes equations are used to treat turbulence-related problems. One is the Direct Numerical Simulation (DNS) method, which solves the equations with a mesh fine enough to allow vortices of any size to be treated explicitly. This approach is certainly the most desirable, but it requires such considerable computational resources that it is rarely used. On the other hand, the method of applying the Reynolds decomposition to the time-averaged Navier-Stokes equations does not simulate fluctuations per se, but it does consider the effect of turbulent fluctuations on the mean flow. Finally, a growing number of applications require an intermediate method known as Large Eddy Simulation or LES, which explicitly represents the largest eddies (carrying the bulk of the energy) and accounts for the contribution of small, low-energy eddy structures through an empirical formulation.

Box 4.5. Meteorology in China

The history of meteorology in China goes back more than three thousand years. During the *Shang* Dynasty (1600-1050 CE), the first observations of natural geophysical phenomena were made. During the *Zhou* Dynasty (1050-256 CE), meteorological archives were created and inscriptions were found on bronze objects and bamboo books. By the time of the *Qin* Dynasty (221-206 CE), the central government of Imperial China was keeping regular reports on rainfall. For much of the country's history, at the instigation of the philosopher Dong Zhongshu (179-104 BCE), natural disasters, which were seen as "warnings from heaven," were examined from a religious and political perspective, forcing the emperor to mourn and support the victims of these extreme events.

In the pre-modern period, the *Ming* Dynasty (1368-1644 CE) encouraged research by Jesuit missionaries, who introduced early observation systems and data analysis techniques. Father Alfonso Vagone (1568-1640) brought a translation of Renaissance writings to China. Fathers Ferdinand Verbiest (1623-1688) and Martino Martini (1614-1661) introduced the thermometer to China. Under the *Qing* Dynasty (1644-1911), observations were made

[184] The equation is solved in terms of the Fourier components of the velocity field.

[185] Orszag, S.A., Patterson, G.S., Jr, Numerical simulation of three-dimensional homogeneous isotropic turbulence. *Physical Review Letters 28*(2), 76-79, 1972.

throughout the country. In 1705, an incident with the emperor put an end to the expansion of Christianity in China and caused the missionaries to leave the country. The Jesuit Society was suppressed in 1773 by order of Pope Clement XIV but restored in 1814 by Pope Pius VII. The Jesuits returned to China in 1842. The French Jesuits established an observatory in Zi-ka-wa, a district west of Shanghai, specializing in typhoon forecasting and the study of geomagnetism. The first ozone measurements in China were made by Father Pierre Lejay (1898-1958), director of this observatory.

After the fall of the *Qing* Dynasty in 1911 and the establishment of the Republic of China (1912-1949), meteorological services were greatly expanded. The number of stations increased rapidly, and a "Central Observatory" was established in Beijing in 1912. However, the modernization process was interrupted by the Sino-Japanese War (1937-1945), and many stations were destroyed.

With the founding of the People's Republic of China in 1949, a "Meteorological Bureau of the Central Military Commission" replaced the "Central Weather Bureau". The latter, established in 1941 and located in Chongqing in western China to escape Japanese occupation, moved to Taiwan with the fall of the Kouo-Min-Tang (Nationalist Party) in 1949. In People's China, the surveillance network was rebuilt and continued to operate during the troubled period of the Cultural Revolution (1966-1976). The prevailing mood under the Communist regime in the 1960s is well summed up in the text written by Chao Chiu-chang, a member of the Institute of Geophysics of the Academia Sinica, from which the following excerpts are taken:

> "In the past decade, under the enlightened leadership of the Communist Party, the Chinese people have courageously marched toward socialism. This decade also marked the rapid development of meteorology. Before the liberation, projects were trying to survive. Since the reactionary government did not emphasize science, meteorology was separated from the masses."
>
> In 1955, meteorological research began in China with the elaboration of a comprehensive development program. [...] In the first half of 1956, over 300 specialists, under the direction of the State Council and the Central Committee of the Chinese Communist Party, together with 18 academics, professors and physicists from the Soviet Union, formulated a twelve-year scientific plan for China. [...] In 1958, on the back of the anti-Rightist movement, the nation launched the Great Leap Forward. To meet the needs of the rapid scientific development of industry and agriculture, Chinese meteorology took part in this great leap forward."

The China Meteorological Administration was established in 1994, bringing together the institutions responsible for weather observation and forecasting. Today, the agency has advanced technological resources.

The development of meteorology in China in the twentieth century benefited from the vision of some outstanding members of the academic world. Some of them had to work under sometimes difficult conditions.

The scientist considered the founder of modern meteorology in China is Zhu Kezhen (1890-1974), also known as Coching Chu. After completing his secondary education in Shanghai, the son of a rice merchant from Shaoxing

enrolled in the Railway and Mining School in Tangshan, Hebei Province, where he graduated as a civil engineer. Thanks to an American scholarship funded by China's reparations to the United States for the Boxer Rebellion of 1900, Zhu left his homeland in 1911 to study geography on the other side of the Pacific. He attended the Universities of Illinois (Urbana-Champaign) and Harvard. He earned a Ph.D. in meteorology from the latter.

Upon his return to China, he taught at Wuchang and Nanjing Teacher Training Colleges, where he established a geoscience department and trained the first generation of meteorologists. In 1928, he became director of the Nanjing Institute of Meteorology, one of eight scientific research institutions established in China by *the Academia Sinica*. At that time, Nanjing was the capital of the Republic of China. From this institute, which is considered the predecessor of today's Beijing Institute of Atmospheric Physics, Zhu Kezhen developed a nationwide network of weather observation stations.

In 1936, Kuomintang nationalist leader Jiang Jieshi (1887-1975), better known in the West as Chiang Kai-shek, asked Zhu to head Zhejiang University in Hangzhou, which became one of China's most prestigious universities. After the Communists seized power in 1949, Zhu refused to follow the Kuomintang leader to Taiwan and took refuge in Shanghai to avoid reprisals from Nationalist agents. He joined the new regime and became vice president of the Academy of Sciences, in charge of geophysics and biology. This new position allowed him to establish several institutes, including the Institute of Oceanology in Qingdao. Zhu also chaired the Chinese National Committee for the International Geophysical Year (IGY, 1957-1958, see Chapter 5). Discussions were difficult because of the political problems between Communist and Nationalist China. Zhu announced that the People's Republic of China was withdrawing from the IGY because the Council of Scientific Unions had accepted Taiwan as a participant in this major international project. In 1972, Zhu published a *Preliminary Study of Climate Change Over the Last 5000 Years*, which is considered a masterpiece.

Tu Changwang (1906-1962) also played a leading role in the development of meteorological measurement and forecasting systems in China. Educated at London's Imperial College in the 1930s, he returned to his homeland at the express request of Zhu Kenzhen and later became head of the Meteorological Administration of the Central Military Commission of the Chinese Communist Party. In this role, he developed long-term weather forecasting programs, established regional weather bureaus throughout the country, and brought meteorology closer to the business community. He was directly involved in the establishment of the renowned meteorology school that is now the Nanjing University of Information Science and Technology (NUIST). He trained the first group of students to work on climate-related issues. He died prematurely at the age of 56.

Another Chinese scientist played a major role in the development of atmospheric and geophysical sciences. This was the meteorologist Zhao Jiuzhang (1907-1968), also known as Jeou Jang Jaw. Zhao is considered the father of China's artificial satellite programs. Born into a family of physicians, this lover of classical poetry and passionate student of physics was drawn closer to his comrades who embraced a progressive vision of society, forcing him to

flee to his hometown of Wuxing in 1925 to avoid reprisals from the military leadership. In 1927 he joined the Communist Youth League, and two years later he was admitted as a student to Tsinghua University in Beijing, where Zhu Kenzhen was one of his professors. He earned a Ph.D. from Berlin's Humboldt University in the 1930's and returned home to become head of the meteorology department at Tsinghua and, in 1944, director of a similar institute at the Academia Sinica. After the defeat of the Nationalist Party and the victory of the Communist forces in 1949, he refused to emigrate to Taiwan and joined the Academy of Sciences established by the new regime in 1949.

In the 1950s, Zhao Jiuzhang became interested in the development of artificial satellites and, following the launch of Sputnik in Russia in 1957, suggested that a Chinese space exploration program be launched. Mao agreed, but progress was slow because China's priority was to develop missiles and the atomic bomb. Zhao went to Moscow to propose cooperation with the Soviets, but received a frosty reception: the USSR was unwilling to share its space technology. So China had to go it alone. By 1964, the conditions were ripe for putting a Chinese satellite into orbit. Zhao was put in charge



FIGURE 4.40: From left to right and top to bottom: Zhu Kezhen (1890-1974), Zhao Jiuzhang (1907-1968), Tu Changwang (1906-1962) and Ye Duzheng (1916-2013).

of the project, which was scheduled for completion in 1970-1971. A special institute, headed by Zhao, was set up to build and launch the satellite, called "Dongfanghong-1". Then came the Proletarian Cultural Revolution (1966-1976), and Zhao was gradually relieved of his responsibilities. He was no longer allowed to follow the development of the project he had conceived, which depressed him deeply. However, he was supported by Prime Minister *Zhou Enlai*, who invited him to attend the Labor Day celebrations on May 1, 1968. The invitation letter, which was probably confiscated, never reached him. Taken to task by the Red Guards, Zhao Jiuzhang committed suicide on October 10, 1968. The satellite he envisioned was launched on April 24, 1970.

Finally, Academician Ye Duzheng (1916-2013) laid the scientific foundations of atmospheric physics and dynamics in China. A former student of Carl-Gustav Rossby, Ye graduated from Tsinghua University in Beijing in 1940, studied at Zhejiang University in Hangzhou from 1940 to 1943, and received his Ph.D. from the University of Chicago in 1948. He was also interested in the meteorology of the Tibetan Plateau. In 1978, he was appointed director of the prestigious Institute of Atmospheric Physics of the Chinese Academy of Sciences, and devoted himself to the study of climate dynamics and the interactions between the atmosphere, hydrosphere, and biosphere. An advocate of international cooperation, he contributed to the development of several programs, including the World Climate Research Program and the International Biosphere-Geosphere Program. In 1984, he was probably the first Chinese scientist to take an interest in global change and promote the concept of sustainable development.

Technological Revolution and Atmospheric Observation

During the first half of the twentieth century, meteorology evolved from a long-standing empirical science into a rational science based on the concepts of fundamental physics. The translation of these concepts into a mathematical formalism and the introduction of numerical methods to solve the equations of fluid mechanics led to an extraordinary improvement in weather forecasting. The introduction of electronic computers since the 1950s and the dizzying increase in available computing resources have contributed to the progress we have seen in recent decades, although statistical methods, interpolation techniques, and empirical laws are still available to the forecaster to refine the predictions provided by numerical models. Today, artificial intelligence has also been introduced to improve or downscale weather forecasts.

Despite the tremendous theoretical advances made by pioneers such as Bjerknes, Rossby, Charney, von Neumann, and Lorentz, improvements in weather forecasting would not have been so significant without the daily contribution of observations. The proliferation of weather stations around the world, the development of communications networks that allowed forecasting centers to exchange information by telegraph, teletype, and facsimile, and the use of radiosondes to measure meteorological parameters at altitude all contributed to the advances that began in the 1920s. However, the real technological revolution

that turned weather services upside down was the introduction of radar in the late 1940s and satellites in the 1960s. The first meteorological satellite, TIROS, launched by the Americans less than three years after the Soviet launch of Sputnik, made it possible to monitor the evolution of cloud systems, especially in regions without ground stations. Today, geostationary satellites located above the equator and scanning a large area of the Earth provide very high-resolution information several times an hour. Finally, using remote sensing techniques, satellites provide precise information on vertical profiles of air temperature and humidity, as well as the location and nature of precipitation zones.

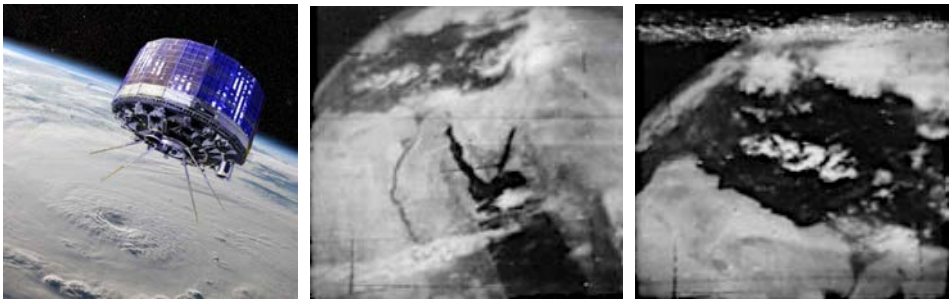


FIGURE 4.41: Representation of the first TIROS weather satellite launched by the United States on April 1, 1960, and first images from the satellite. Note the Dead Sea in the center (dark) and the presence of clouds in the region, including over the Egyptian desert. On the right, clouds in the center of the Mediterranean Sea and over Europe. Sources: European Space Agency and NASA.



FIGURE 4.42: A thunderstorm system photographed from the International Space Station.

In short, the quality of weather forecasts based on numerical simulations has gradually improved thanks to the increasing number of observations used to determine the initial conditions used in atmospheric models. The assimilation of observations into these models makes it possible to optimally combine measurements with the constraints of fluid dynamics. Access to high-performance computers has made it possible to increase the spatial resolution of meteorological models, i.e., to adopt a numerical grid much finer than that envisaged by Richardson in his first attempt to predict the evolution of the meteorological situation. Today, meteorological agencies such as ECMWF (European Center for Medium-Range Weather Forecasts) in Europe, UK Met Office, Meteo-France, DWD (Deutsche Wetterdienst) in Germany, NOAA (National Oceanographic and Atmospheric Administration) in the USA, MSC (Meteorological Service of Canada), CMA (China Meteorological Administration) in China, JMA (Japan Meoteorological Agency) in Japan, KMA (Korea Meteorological Administration) and other centers provide daily global weather forecasts at a horizontal close to 10 kilometers. Another source of progress is the improved formulation of the physical processes that generally occur on small time and space scales, including the representation of convective exchange, cloud development, precipitation formation, and turbulent exchange in the atmospheric boundary layer.

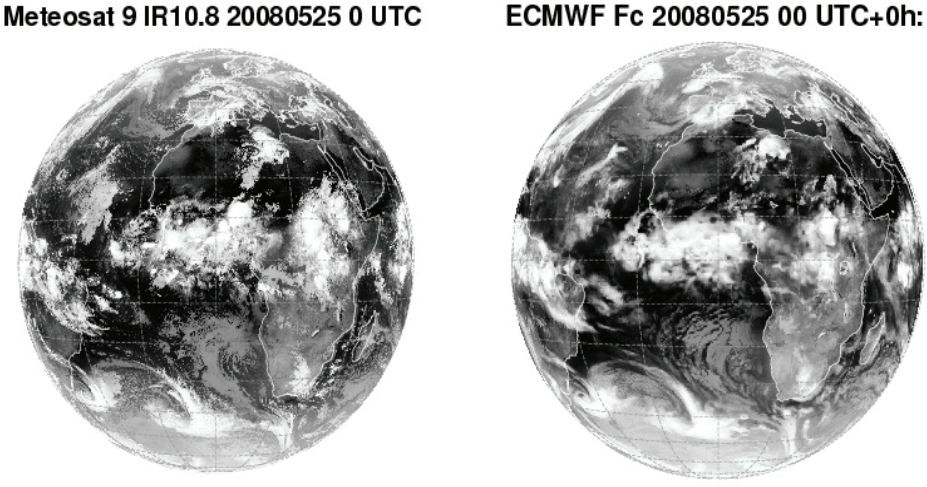


FIGURE 4.43: Right: Cloud cover forecast by the European Center for Medium-Range Weather Forecasts for 25 August 2008 at 0 UTC. Left: Observation of the cloud layer by the Meteosat 9 satellite (infrared measurements) at the time corresponding to the forecast.

Finally, it should be emphasized that atmospheric models are ideal tools for simulating the transport of gases and liquid or solid particles by atmospheric circulation, as well as their transformation by chemical reactions or physical processes. They are therefore used today to simulate the global or regional distribution of chemical species in the atmosphere and, for example, to predict air pollution levels in urban areas. We will return to chemistry and transport models in Chapter 8.

5
The Upper Layers of the Atmosphere

The advances made by researchers since the Renaissance have made it possible to identify the most abundant gases in our atmosphere. The pioneers of the study of the chemical composition of the air were mainly interested in the processes taking place near the surface and in the lower layers of the atmosphere. Measurements from balloons that occasionally penetrated the stratosphere showed that the ratio of nitrogen to oxygen is invariant with altitude, at least up to 30 km above sea level. But is this always the case at higher altitudes? Before the middle of the twentieth century, there was no way to study the atmosphere above the altitude reached by balloons. Research was therefore based on theoretical studies that could not be verified experimentally. In a book published in 1914, Alphonse Berget[186] summed up the state of science with these words:

> "It is at an altitude of 75 to 80 kilometers that, according to the new views of physicists, the region of discontinuity in the constitution of the atmosphere begins; at this altitude the total pressure of the air found there is only a quarter of a millimeter, and 50% of this air consists of hydrogen. At 90 km, the infinitesimal amount of air at this altitude should be 70% hydrogen, and at 100 km, 99.5% hydrogen, 0.4% helium, and 0.1% nitrogen; oxygen must be completely absent at this altitude."

In the following years, however, these results were completely challenged by information obtained from the analysis of two physical phenomena observed from the Earth's surface: the formation of polar lights and the propagation of radio waves in the atmosphere. In the second half of the twentieth century, rockets and satellites provided additional information.

[186] Baron Thomas Claude Xavier Alphonse Berget (1860-1933) was a French geophysicist and oceanographer, author of a large number of works on meteorology and oceanography.

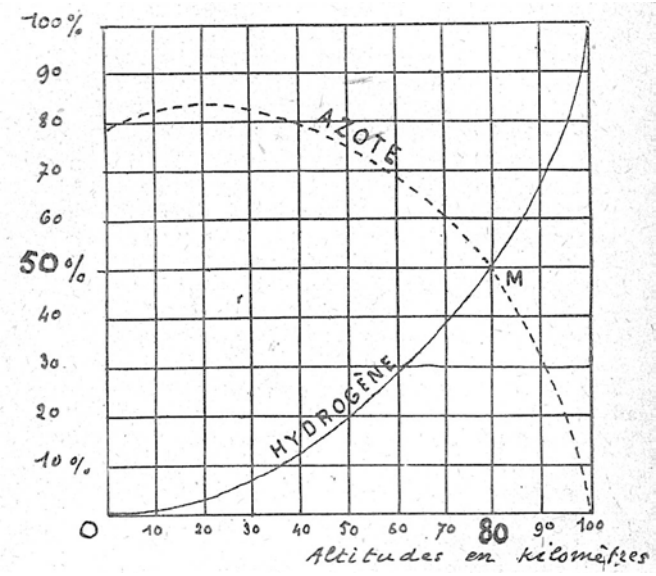


FIGURE 5.1: Proportion of nitrogen and hydrogen (in percent) as a function of altitude (in kilometers), as imagined by scientists at the beginning of the twentieth century and presented in A. Berget's 1914 publication. In this theoretical model, it is assumed that the proportion of hydrogen is equal to that of nitrogen at an altitude of 80 km, and that oxygen is completely absent above this level. Observation will show that this model does not correspond to reality. Source: A. Berget, Les problèmes de l'atmosphère, 1914.

The Polar Aurora

Polar lights have fascinated people since ancient times. These majestic curtains of light are mentioned in the Old Testament but were perhaps first described in 2600 BCE by Fu-Pao, the mother of the legendary Chinese emperor Xuan-Yuan, nicknamed the Yellow Emperor, who noted the appearance of a strong luminosity in the sky around the star Su in the Beidou constellation. Throughout history, the lights of the night sky have captured people's imagination, creating legends and myths around them. In the polar regions, where auroras are most common, the Inuit of Greenland, who call auroras *aqsarniit*, believed that the lights in the night sky were produced by the souls of humans playing ball with walrus skulls. In the imagination of some people, the phenomenon was a harbinger of misfortune, disaster, and disease. This was the case in Europe during the Middle Ages: the red hue of the aurora was associated with war and blood. For others, the appearance of the aurora heralded a period of prosperity and good fortune. The Japanese, for example, believed that children born at dawn are destined to be intelligent and successful.

The first rational analyses beyond mythical beliefs came from the ancient Greeks with the writings of the philosophers Anaximenes of Miletus (585-528 BCE) and Xenophanes of Colophon (~570-475 BCE). Two centuries later, Aristotle evoked the northern lights of the sky in his book *Meteorologica*. However, it wasn't until

the seventeenth century that the term "*Aurora Borealis*" was mentioned in Galileo's correspondence of 1620, unless, as some believe, it was the French philosopher, Catholic priest, and freethinker Pierre Gassendi (1592-1655) who introduced the term[187]. In any case, the term Aurora is derived from the Roman name of the Greek goddess of dawn, who represented the eternal alternation of day (light) and night (darkness), and the word Boreas personifies the "north wind" in mythology.

The light of the night sky has not only been observed in the northern hemisphere. In 1773, English explorer James Cook (1728-1779), a Royal Navy captain leading an expedition to Australia aboard the ship *Endeavour*, noticed the appearance of phenomena very similar to the aurora borealis. Cook thus discovered the presence of the *aurora australis* in the southern hemisphere.

At the end of the 18th century, Henry Cavendish used triangulation to determine that the aurora observed on February 23, 1784, was located between 83 and 115 km above sea level. Seventy-five years later, the mathematician Elias Loomis (1811-1889), a specialist in terrestrial magnetism, professor at the City University of New York and later at Yale University, and founder in 1838 in Hudson, Ohio, of one of the oldest astronomical observatories in the United States, organized a major expedition to the Arctic. In particular, he studied an auroral episode from August 28 to September 4, 1859. These observations, together with other data at his disposal, enabled him to determine the geographical distribution of the aurora and to draw up a first map of its frequency of occurrence. This map showed that the aurora occurs most frequently in a

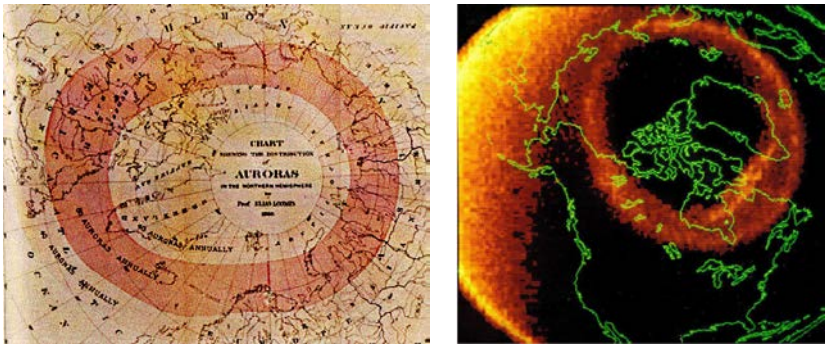


FIGURE 5.2: Left: The first map showing the annual frequency of polar auroras, drawn by Elias Loomis in 1860. The dark oval corresponds to a frequency of more than 80 auroras per year. Source: E. Loomis. Right: Representation of the auroral oval in the polar region of the Northern Hemisphere observed in the ultraviolet on November 8, 1981 by the photometer developed at the University of Iowa and carried aboard the Dynamics Explorer-1 satellite. The observed emission comes mainly from emission lines of atomic oxygen at wavelengths of 130.4 and 135.6 nm and emission bands of molecular nitrogen.

[187] A philosopher, astronomer, mathematician, and Catholic priest born in Provence, Pierre Gassendi (1592-1655), or Petrus Gassendin, taught in Digne and Aix before accepting a chair at the Collège Royal de France in 1645 and joining the group of freethinkers in the French capital. A proponent of theories that advocated skepticism and empiricism in scientific work, he came into conflict with René Descartes, who believed that the search for truth should be based on rationality.

"ring" centered around the Earth's magnetic pole. This ring was observed from space in the early 1980s by NASA's Dynamics Explorer-1 satellite.

Despite the available observations and the stories of indigenous peoples who have scanned the skies for centuries, there were still questions that scientists must answer: What are the mechanisms that produce light in the night sky, especially in the polar regions? And what do the auroras tell us about the chemical composition of the air in the upper layers of the Earth's atmosphere?

The large number of auroras observed in Europe in the eighteenth century not only aroused real concern among the population but also aroused the curiosity of learned societies eager to reassure minds with rational explanations. The Royal Society in London and the Académie royale des sciences in Paris invited the English astronomer Edmond Halley (1656-1742) and the French physicist Jean-Jacques d'Ortous de Mairan (1678-1771), respectively, to study the question of the aurora borealis. The two scientists had very different views on the subject. Halley, who studied the spectacular event of May 6, 1716, considered the aurora to be essentially an atmospheric phenomenon generated by the Earth, which he imagined to be an immense magnet characterized by the existence of two magnetic poles located near the geographic poles. He invoked magnetic currents emanating from these poles, which behaved like iron filings around the magnet. This theory, which dates back to 1716 and was supported in 1741 by the Swedish astronomer Anders Celsius (1701-1744), noted that the needle of a compass is disturbed when an aurora appears. However, these studies offered little insight into the precise mechanism behind the formation of the aurora. They did, however, link the formation of auroras to the existence of the Earth's magnetic field, which helped explain the frequent presence of auroras in the polar regions and the relationship observed by the German explorer von Humboldt between the frequency of their appearance and geomagnetic activity. The German scientist considered auroras to be "magnetic storms" and wrote in 1855:

> "The appearance of the aurora borealis is the act that puts an end to a magnetic storm, just as in electrical storms a phenomenon of light, the flash, announces that the momentarily disturbed equilibrium in the distribution of electricity has finally been restored. The storm is usually confined to a small area, outside of which the electrical state of the atmosphere has not been disturbed. Magnetic storms, on the other hand, extend their influence over a large part of the continents."

This atmospheric theory was opposed by Mairan's cosmic theory, presented in 1733. The French astronomer believed that the cause of the aurora was the zodiacal light, i.e. the solar atmosphere. He referred to a very thin fluid, visible only during solar eclipses, which he believed was subject to the gravitational attraction described by Isaac Newton. In 1754, he wrote[188]:

> "It is certain [...] that the atmosphere of the Sun, seen as zodiacal light, sometimes reaches the orbit of the Earth and beyond. It is then that the matter of which this atmosphere is composed, after encountering the upper parts of our

[188] de Mairan, J.-J. d'O. *Traité physique et historique de l'aurore boréale*, Seconde édition revue et augmentée de plusieurs Éclaircissements, Imprimerie Royale, 448 pp., 1754.

> air, below the limits where universal gravity begins to act with greater force towards the center of the Earth than towards the Sun, falls into the Earth's atmosphere at a greater or lesser depth, depending on whether the specific gravity is greater or lesser with respect to the layers of air through which it passes or on which it is supported."

This theory was criticized by Leonhard Euler, who refuted the idea that the Sun's atmosphere could extend to the Earth. Instead, he believed that the reflection of the Sun's rays off auroral matter explained the formation of light in the night sky. The French physicist and astronomer François Arago (1786-1853), who rejected Laplace's Newtonian theory of gravity and was aware of the newly established laws of electromagnetism, insisted on the close connection between the aurora and magnetism.

It wasn't until the work of physicist Kristian Olaf Bernhard Birkeland (1867-1917) that the role of the Earth's magnetic field in the formation of auroras was understood. Birkeland was born in Christiania (now Oslo), Norway. After completing his studies in physics, chemistry, and mathematics, supplemented by stays in France where he met Henri Poincaré, he became a member of the Norwegian Academy of Sciences and a professor at the Royal Frederick University in Oslo. In 1899 and 1900, he organized several expeditions to the polar regions to study the magnetic field where auroras are most common. He deduced the existence of electric currents in the form of electric jets[189] aligned with magnetic field lines. Birkeland took up the idea developed three hundred years earlier by the English physician William Gilbert (1544-1603) in his work published in 1600: *De Magnete, Magneticisque Corporibus, et De Magni Magnete Tellure*[190]. At the time of the first studies of terrestrial magnetism, Gilbert had proposed to equate the Earth with a magnet, arguing that the magnetized needle of a compass sensitive to the magnetic field would always point north. The English physicist, sometimes considered the father of modern electricity, had developed a "reduced model" of the Earth around a magnet, which he called *Terrella* (the small Earth). Birkland adopted this representation, but this time to better visualize the relationship between the Earth's magnetic field and the formation of auroras. His "reduced model" consisted of a sphere containing a magnet that defined the position of the north and south magnetic poles on the sphere. The sphere was suspended in an empty enclosure. The Norwegian scientist studied the behavior of the cathode rays (i.e., electrons) that he injected into the enclosure, which was exposed to the Earth's magnetic field generated by the magnet. He found that the electrons did indeed follow the lines of this field, converging in the regions near the magnetic poles and forming rings around them, similar to the ovals associated with the formation of auroras in the polar regions.

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[189] "Electrojets" are electric currents produced by the displacement of charged particles (mainly electrons) in the Earth's upper atmosphere between 80 and 150 km altitude. These currents, highly concentrated in latitude, are permanently observed along the magnetic equator. They also occur around the polar regions during auroras and following other magnetic disturbances. In the latter case, we speak of "auroral electrojets".

[190] Magnetism and magnetic bodies, and the great Earth magnet.

Following his work and in his book *The Norwegian Aurora Polaris Expedition 1902-1903*, Birkeland proposed the existence of a plasma that fills the universe:

> "It seems a natural consequence of our views to suppose that all space is filled with electrons and flying electric ions of all kinds. We have assumed that every stellar system, as it evolves, throws electric corpuscles into space. It does not seem unreasonable, therefore, to suppose that the greater part of the material masses in the universe are not found in the solar systems or in the nebulae, but in 'empty' space."

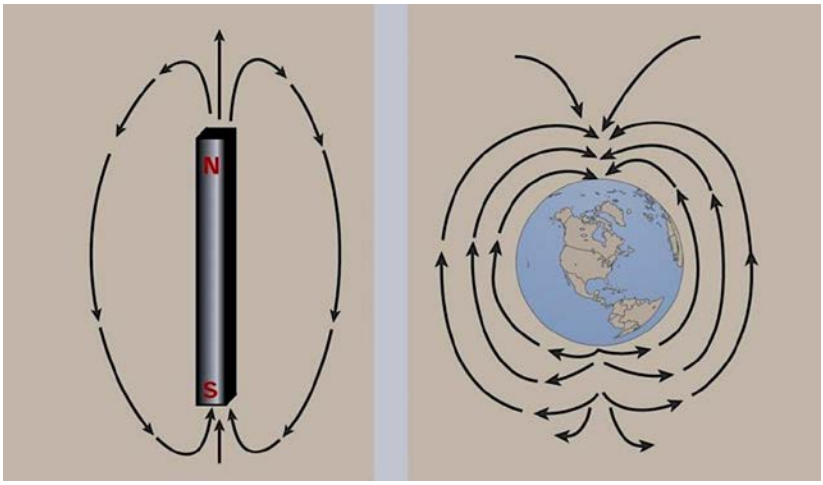


FIGURE 5.3: Analogy between the Earth's magnetic field and the magnetic field generated by a magnet.

The Norwegian astrophysicist and mathematician Fredrik Carl Størmer (1874-1957), fascinated by Birkeland's experiments, decided in the early twentieth century to use a mathematical model he had developed to simulate the trajectory of charged particles subjected to a magnetic field around a sphere. He showed that some of these particles could be trapped by the geomagnetic field and remain confined within a belt surrounding the Earth[191]. Størmer's discovery was confirmed in 1958 by the Explorer-1 satellite's observation of what became known as the Van Allen belts[192]. Størmer's work on the motion of charged particles led to a better understanding of the mechanisms behind the formation of auroras.

[191] Størmer's work is presented in two books, *From the Depths to the Heart of the Atom* and *The Polar Aurora*, Oxford, 1955.

[192] James Van Allen (1914-2006), American physicist and astronomer. From 1951, professor at the University of Iowa and head of the Department of Physics and Astronomy. Thanks to measurements made by the Explorer-1 satellite in 1958 during the International Geophysical Year, Van Allen discovered the presence around the Earth of belts containing energetic charged particles from the solar wind. These belts extend several tens of thousands of kilometers above 700 km altitude.

We now know that the particles ejected by the sun are not only electrons but also protons and alpha particles (helium nuclei). This *solar wind*[193] tends to distort the Earth's magnetic field, compressing it on the Sun's side (day side) and stretching it on the opposite side (night side). This intermediate zone between the atmosphere and interplanetary space, dominated by the Earth's magnetic field, is known as the *magnetosphere*. This invisible barrier surrounding the Earth protects us from the bombardment of charged particles generated by the Sun. Particles trapped in this layer and undergoing an acceleration process can gain enough energy to penetrate the two auroral ovals surrounding the Earth's magnetic poles and interact with the chemical constituents of the atmosphere. The frequency and intensity of the auroras are modulated by the 11-year solar activity cycle (Box 5.1).

Box 5.1. Solar Activity

Thanks to the astronomical telescope he built in 1609, which allowed him to confirm Copernicus' theory of heliocentrism, Galileo observed the presence of dark spots on the shining surface of the Sun. How could this phenomenon, which contradicted the dogmas of Aristotelian physics and in particular the immutability of the stars, be explained? Various hypotheses were put forward: it could be the shadow of certain planets, or dark mountains piercing the Sun's atmosphere, or even the dark, cold surface of the Sun, seen through large openings in the Sun's brilliant atmosphere. Galileo refuted

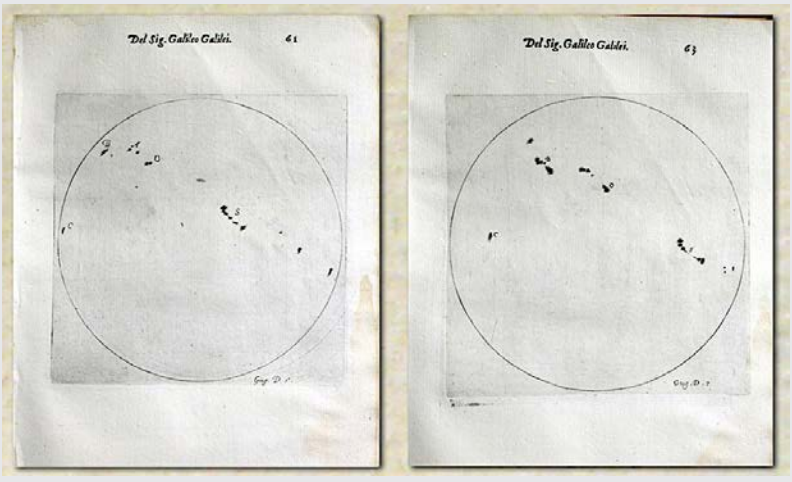


FIGURE 5.4: Galileo's drawings of sunspots © DR.

[193] Introduced in 1955 by American astrophysicist Eugène Newman Parker, the term refers to the flow of charged particles (plasma) emitted continuously by the Sun. The particles propagate through the interplanetary medium at supersonic speed. The solar wind interacts with the obstacles it encounters in its path, and in particular with the Earth's magnetic field, which provides protection for the planet. The solar wind intensifies during periods of high solar activity.

these hypotheses, believing that the ever-changing spots represented clouds in the Sun's atmosphere.

Two centuries after Galileo's work, Samuel Heinrich Schwabe (1789-1875), a pharmacist with an interest in astronomy who practiced in Dessau, a small town along the Elbe, tried unsuccessfully to identify a planet close to the Sun. On this occasion, he discovered that the number of sunspots varies with a period of around 10 years. This discovery, which initially went unnoticed, prompted Johann Rudolph Wolf (1816-1893), Director of the Bern Observatory, to make systematic observations of the Sun's surface. The Swiss astronomer confirmed the existence of a solar cycle, for which he determined a period of 11.1 years.

In England, the amateur astronomer Richard Christopher Carrington (1826-1875), who had studied at Trinity College, Cambridge, discovered the existence of flares on the surface of the Sun, observing in particular the gigantic flare of September 1, 1859. He also noted that the apparent number of sunspots varies with a period of 27 days as a result of the Sun's rotation.



FIGURE 5.5: Protuberance during the September 8, 2010 solar flare observed by NASA's Solar Dynamics Observatory (SDO). NASA/SDO.

Does solar activity affect the Earth's atmosphere? Since the launch of the first artificial satellites in 1957, and in particular the measurement of their drag through the atmosphere, we know that the density of the air, which is sensitive to temperature and therefore to the solar energy input, varies considerably with the 11-year cycle above 150 km altitude. The analysis of the variability of the solar spectrum shows that the intensity of the short-wave radiation (ultraviolet and X-rays), which significantly influences the chemical composition of the upper atmosphere, varies strongly with the solar activity. On the other hand, visible radiation, which plays an important role in the photochemistry of the lower layers of the atmosphere and significantly affects the energy balance of the climate system, is not very sensitive to solar activity.

Polar auroras are most likely to form and spread geographically during periods of high solar activity. Dark spots in the Sun's luminous layer (known as the *photosphere*) are not the only phenomena that contribute to the appearance of auroras. The ejection of particles from the Sun's outer layer, known as the *solar corona*, leads to the formation of magnetic storms and the appearance of auroras even at mid-latitudes.

Kristian Birkeland was an inquisitive and dedicated scientist. He was nominated for the Nobel Prize seven times but was never successful. In addition to his work on the upper atmosphere, he was interested in a wide range of other topics, including the development of an electromagnetic cannon for military purposes and the development of a device to fix nitrogen in the air from a giant artificial lightning bolt to artificially produce fertilizer. But Birkeland was also a tortured mind suffering from paranoia. Only 49 years old, he was found dead in his hotel bed in Tokyo after a scientific mission during which he had taken an excessive dose of barbiturates. A revolver was found on the nightstand next to his bed.



FIGURE 5.6: Kristian Birkeland.

Although Birkeland's work on the existence of electrojets was disputed by several scientists of the time, including geophysicist Sydney Chapman (1888-1970) and Swedish plasma specialist Hannes Alfvén (1908-1995), satellite observations made 50 years after Birkeland's death confirmed the existence of electric currents aligned with geomagnetic field lines.

By the beginning of the twentieth century, it was accepted that the interaction of the solar wind with the Earth's magnetic field was an important mechanism in the formation of polar auroras. However, the processes responsible for the appearance of these majestic curtains of multi-colored light in the night sky, especially in the polar regions, were still not fully understood. How is light produced? And what can the aurora tell us about the chemical composition of the upper atmosphere?

The Mystery of the Green Line

It took several decades before these questions were finally answered. The first important step toward understanding the mechanisms that produce auroral light was made in 1868, thanks to the work of Anders Jonas Ångström (1814-1874). This Swedish scientist studied at the University of Uppsala and became familiar with astronomy during stays at the Stockholm and Uppsala Observatories. After being appointed to the chair of physics at his *alma mater* in 1858, he developed

a program in spectroscopy, a promising new discipline of which he was one of the initiators. Using the spectroscope he built, Ångström observed the solar spectrum in great detail, identifying over a thousand spectral lines. His work would serve as a reference for many years to come. By studying these spectra, he was able to determine the presence of hydrogen in the solar atmosphere.

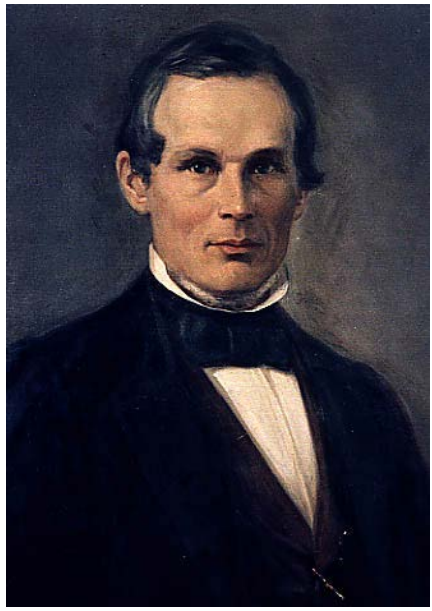


FIGURE 5.7: Anders Jonas Ångström.

Angström also analyzed the spectrum of an aurora borealis, revealing an intense green line whose wavelength he estimated to be 5567 Å (1 Å = 1 Ångström = 0.1 nm). This wavelength was slightly inaccurate, however, because he used a standard meter in his experiments that differed slightly from the international reference based on the Paris standard meter. A later, more precise determination shows that the wavelength of the line is 5577 Å (557.7 nm). This observation provided important information about the physical and chemical conditions in the upper layers of the atmosphere. It was first necessary to determine the origin of this line. This was the subject of much debate and controversy among scientists of the time.

There were many hypotheses to explain the origin of the green line. Some speculated that it is the signature of hydrogen, or perhaps nitrogen or oxygen, in the upper atmosphere. However, no one in the laboratory was able to produce this line from these three chemical species. Some suggested that krypton, which has a line at a wavelength (5570.4 Å) close to the green line, was responsible for the observed light emission, but again, the explanation was not very credible.

Faced with these repeated failures, a new idea began to emerge: the green line could be due to emission from helium, a light gas probably present in large quantities at high altitudes in the Earth's atmosphere. This chemically inert compound was identified in the solar atmosphere in 1868 by the French astronomer Jules Janssen (1824-1907). During a total solar eclipse, he detected the yellow helium line (587.49 nm) emitted by the Sun's corona. The presence of this gas in the Earth's atmosphere was discovered by Sir William Ramsay. However, other hypotheses were proposed. In 1870, the American astronomer Charles Augustus Young (1834-1908) attributed the green line of the aurora borealis to a gas that originated in the solar corona but had not yet been observed in the Earth's atmosphere. He based his hypothesis on the observation of a green solar line with a wavelength of 530.3 nm, very close to the wavelength detected by Ångström. This hypothetical gas was named coronium by the Austrian mathematician Anton Karl Grünwald (1838-1920) in 1887. However, this line was later attributed to the emission of an iron ion present in the solar atmosphere. Another failure.

A few years earlier, in 1869, while working at the Harvard Observatory, the American philosopher and mathematician Charles Sanders Peirce (1839-1914), known for his theories of pragmatism, proposed another original idea: the green line would be due to the emission of a then unknown chemical element whose atomic mass would be less than that of hydrogen. Inspired by an article by the English chemist Henry Roscoe[194], Peirce wrote[195]:

> "The spectrum of the aurora, as usually seen, consists of a single yellowish-green line, which belongs to no substance with which we are acquainted. As the aurora is held to be above the ordinary atmosphere (and this is confirmed by its showing no nitrogen lines), it follows that there is some unknown gas reaching above the other constituents of the atmosphere. According to the laws of gravity and of diffusion of gases, this substance must extend down to the surface of the earth. Why, then, have not chemists discovered it?"

The German meteorologist and astronomer Alfred Wegener (1880-1930), a specialist in the polar regions, observed that the intensity of the green line increased with the altitude at which it was emitted, and deduced that the emission of light must be due to a gas that is only present in large quantities at high altitudes. As in the upper atmosphere of the Sun, there must be a layer of gas around the Earth containing the element responsible for the emission of the green line. According to Wegener, this previously unknown chemical element, which he called *geo-coronium*, is an inert, monoatomic gas with a molecular mass of 0.4. Since this gas is dispersed throughout the atmosphere, its concentration in the troposphere would be on the order of 5.8 parts per million in volume (ppmv). Chapman pointed out, however, that such a light gas, presumably in high proportion at high altitudes, must quickly escape into space. He thought it unlikely that the atmosphere could retain geo-coronium for more than a year. Once again, the hypothesis - this time Wegener's - was unconvincing, and the scientific community, unable to solve the mystery of the Green Line, was in deep trouble. This confirmed the views of Heinrich Kayser[196] who wrote in 1910:

> "We know nothing at all about the chemical origin of polar light lines."

A few years later, in 1923, another suggestion was developed by Norwegian physicist Lars Vegard (1880-1963), an assistant to the famous aurora borealis specialist Kristian Birkeland. Vegard disputed the idea that the green line should be attributed to an unknown gas. On the contrary, he was convinced that this emission was produced by an electrified layer at high altitude, containing fine particles of solid nitrogen. This line, he explained, was produced in the laboratory when he exposed such particles to cathode rays, provided that the temperature was below 35 K. This temperature condition led British scientist

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[194] Text quoted in Kragh, H., Auroral chemistry: The Riddle of the Green Line. *Bulletin for the History of Chemistry*, *35*(2), 97-104, 2010.

[195] Charles Sanders Peirce: Published Works I., Part One: 1869-1893, Volume 1 Charles sanders Pierce: contributions to the nation: 1869 (22 July 1869) 73-74: Roscoe'e spectrum analysis.

[196] Kayser, H., *Handbook der Spectroscopie*, *5*, Hirzel, Leipzig, 1910.

Gordon Dobson to reject this hypothesis since the temperature of the upper atmosphere should be much higher than 35 K. Still no satisfactory answer!

It was not until the emergence of atomic physics and quantum mechanics that decisive progress was made. It was at the University of Toronto in Canada that the question posed since 1868 was finally resolved, thanks to the laboratory work of Gordon Merritt Shrum (1896-1985), a "post-doc" of chemistry professor Sir John Cunnigham McLennan[197] (1867-1935). The two Toronto researchers, who also disputed Vegard's theory, were initially convinced, as was Sydney Chapman, that the origin of the green line was related to the presence of helium in the upper atmosphere. Shrum tried to produce the green line from helium, but his first attempts were unsuccessful. In February 1925, he made a final attempt, and this time the green line appeared. To his surprise, further attempts were unsuccessful, but two weeks later the line reappeared. Shrum was extremely frustrated, writing in his autobiography[198] published in 1986:

> "I thought I was going to have a nervous breakdown. At last, I was so desperate that I tried a most unscientific approach. I decided that I would get up at the same hour of the morning as I had on the great day, have the same breakfast, go over to the university at the same hour, put on the equipment in the same way, and look in the tube at exactly the same time. I did all that, looked in, and the line was there."

Why was the formation of the green line random? Shrum finally solved the puzzle, realizing that the helium used in some of his experiments was contaminated by the presence of oxygen and nitrogen. By using a mixture of oxygen instead of helium, he easily produced the green line he was trying to explain.

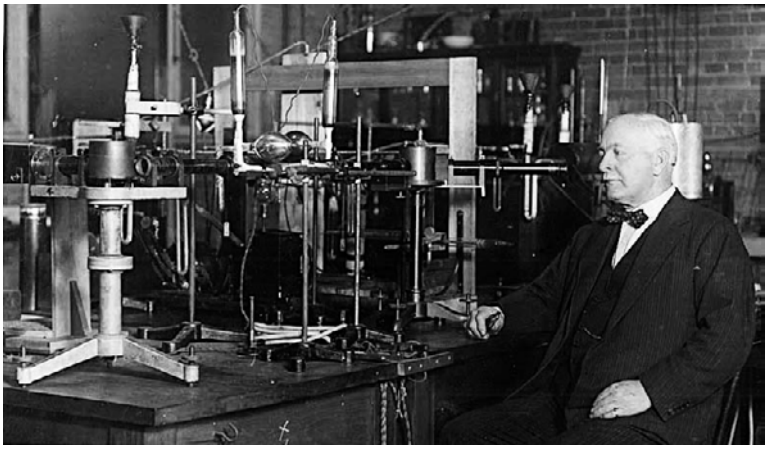


FIGURE 5.8: Sir John McLennan, Director of the Physics Laboratory at the University of Toronto, in front of the apparatus that led to the identification of the green auroral line in 1925. Photo taken in 1928 ©DR.

[197] See the article by Kragh H., The green line: a chapter in the history of auroral physics. *Astronomy & Geophysics*, 2009 - academic.oup.com

[198] Shrum, G., *An Autobiography*, Un. British Columbia Press, Vancouver, 46, 1986.

This is where McLennan came in. Well-versed in the fundamentals of atomic physics, he observed that the wavelength of the green line corresponds to the energy difference between two electronic states of oxygen in its atomic state. The green line therefore, does not represent an emission produced by helium; it is produced by a "forbidden" transition[199] between two metastable states of the oxygen atom. These electronic states are referred to as ^{1}S and ^{1}D (see Box 5.2).

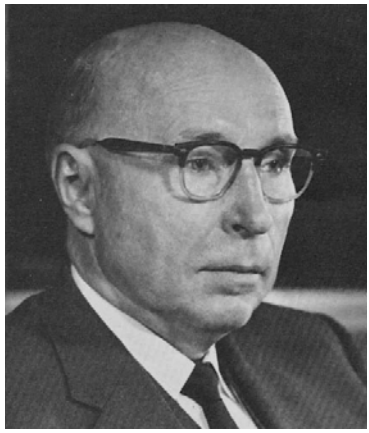


FIGURE 5.9: Gordon Shrum, who identified the green oxygen line.

These results were of the utmost importance because they showed for the first time that atomic oxygen was present in the upper atmosphere. After decades of confusion, this fundamental discovery profoundly changed the course of upper atmosphere research. But it also illustrated the difficulty of the scientific process. The various attempts made over more than half a century to explain the mysterious green color of the aurora were the subject of intense debate among scientists of the time, with rivalries between specialists, doubts, and certainties being called into question a few years later. But in the end, the difficult problem was solved thanks to laboratory studies and theoretical advances in atomic physics and quantum mechanics.

Box 5.2. Radiative Emissions from the Oxygen Atom

The oxygen atom O can exist in three different electronic states: the triplet ground state O(^{3}P), the first excited singlet state (O^{1}D), and the second excited singlet state O(^{1}S). The notations are those used by spectroscopy specialists. In the upper atmosphere, the main source of energy to move this atom from the ground state to one of the excited states is essentially provided by the precipitation in the atmosphere of very energetic magnetospheric electrons. The de-excitation of the oxygen atom (return to a less energetic state) occurs through two different processes, each of which releases energy to the immediate environment. The first results from collisions of the excited atom with atmospheric particles and transfer energy in the form of heat. The second is the emission of photons. As collisions become rarer with decreasing air density, their importance decreases with altitude. Above a certain level, photon emission becomes the fundamental process for restoring the activation energy initially acquired by the atom. The wavelength of the corresponding radiative emission is determined by the energy difference

[199] Energy transitions normally not allowed by the selection rules of quantum mechanics. However, there is a non-zero probability that spontaneous transitions between energy states of an atom or molecule will occur if that atom or molecule is brought to an excited state.

between the two levels between which the transition occurs. The transition from the ^{1}S state to the ^{1}D state produces the "green line" at 557.7 nm, and the transition from the ^{1}D state to the ^{3}P state produces "red lines", the two most intense of which have wavelengths of 630.0 and 636.4 nm, respectively (see figure 5.10). The two excited states ^{1}D and ^{1}S are called metastable because the transitions $^1\text{S} \rightarrow {}^1\text{D}$ (green line) and $^1\text{D} \rightarrow {}^3\text{P}$ (red lines) are nominally forbidden because they violate the selection rules specific to quantum mechanics. As a result, the excited atoms remain frozen in their respective states for a certain period of time. This period, called the radiative lifetime, is 0.84 s (green line) and 114 s (red lines) for O(^{1}S) and O(^{1}D), respectively. The radiative process dominates when the radiative lifetime is shorter than the time required for a collision between the excited atom and an atmospheric particle to occur. This explains why the green line is produced at relatively low altitudes (100-150 km) and the red line appears above 150-200 km. The light intensity associated with the ^{1}S to ^{3}P transition at 297.2 nm is much lower than that of the green line, for example.

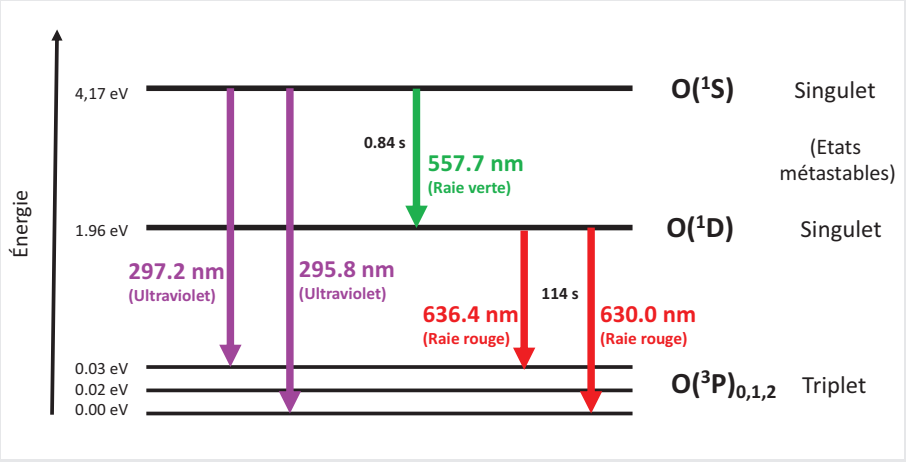


FIGURE 5.10: Energy levels of the oxygen atom with the ^{3}P triplet and the ^{1}D and ^{1}S singlets. The radiative transitions are shown with their respective wavelengths.

In the following years, new spectroscopic studies provided additional information. For example, additional spectral bands were observed in the atmosphere and attributed to the emissions by the nitrogen molecule N_2 excited by collisions with energetic electrons, and by the ionized nitrogen molecule N_2^+. All these studies explain the different colors that characterize the auroras: the green light is produced between 100 and 200 km altitude by the transition between the ^{1}S and ^{1}D states of the oxygen atom; the red light is produced above 200 km by the transition between the ^{1}D and ^{3}P states of the same atom; the purple light is linked to the emission bands of ionized molecular nitrogen; and the much rarer blue light is attributed to the emission bands of molecular nitrogen.

We can summarize what the various studies of the nineteenth and twentieth centuries taught us. After a solar flare, an intense stream of electrically charged particles reaches the magnetosphere, which acts as a protective shield for the Earth. The primary electrons, a component of the solar wind, are then channeled by the Earth's magnetic field lines and end up in the auroral oval. As they penetrate the atmosphere, they transfer their energy to atmospheric atoms and molecules (e.g., oxygen atoms and nitrogen molecules), which can then be excited by shifting electrons to higher energy states. De-excitation is accompanied by the transfer of an electron to a lower energy state, resulting in the emission of a photon[200]. It is these light emissions that make up the aurora borealis and australis.

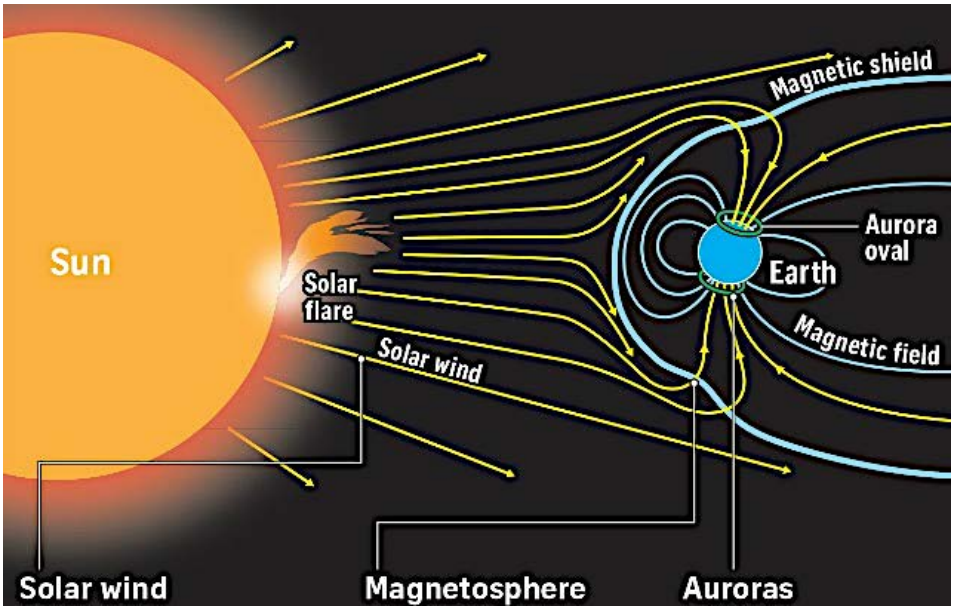


FIGURE 5.11: Schematic representation of the solar wind, composed of electrons and protons escaping from the solar atmosphere and propagating through interplanetary space. These electrically charged particles interact with the Earth's magnetosphere along magnetic field lines. The magnetic shield (blue lines) protects the Earth and its atmosphere from the influence of the solar wind. However, the most energetic particles are able to penetrate this shield and reach the Earth's polar regions, particularly in the auroral oval. Source: Les Géologues du Maroc.

Nightglow or Airglow

Auroras are not the only light-producing phenomenon in the night sky. In fact, even in the absence of this intense phenomenon, and in the absence of direct light from the moon and stars, a faint glow is produced by the atmosphere itself.

[200] The elementary particle that makes up light.

At the suggestion of the American geophysicist Christian Thomas Elvey (1889-1970), this light from the sky is called *airglow*. Unlike the radiation produced by auroras, which occurs mainly at high geomagnetic latitudes - the only regions accessible to solar wind particles and magnetospheric electrons - airglow is a continuous, amorphous emission present at all latitudes. Like auroral emission, airglow is mainly produced by atomic and molecular transitions, but the excitation processes are different, resulting from ionization, recombination, and photochemical reactions.

As in the case of auroras, the main radiative emissions observed at night are the green and red lines of atomic oxygen. In the case of the airglow, the energy input leading to the excitation of the oxygen atom results from a reaction between two oxygen atoms leading to the formation of an oxygen molecule in an excited state; this molecule, through a collision in the atmosphere, transfers its excess energy to an oxygen atom in the ground state $O(^3P)$, leading to the formation of an excited atom $O(^1S)$[201]. The de-excitation of $O(^1S)$ produces the emission of the green line. Several mechanisms, such as the collision of a high-energy electron with an $O(^3P)$ oxygen atom, produce the $O(^1D)$ atom, and its radiative transition to the ground state produces a red line doublet.

Other chemical species in the atmosphere were identified through a more comprehensive analysis of the airglow's spectral signatures. The intense emission of a yellow line at 589 nm indicated the presence of the sodium atom in the upper atmosphere. The sodium layer, discovered in 1929 by the American astronomer Vesto Shipher (1875-1969) of the Lowell Observatory in Flagstaff, Arizona, is formed at an altitude of about 100 km by the ablation of meteors (solid bodies of extraterrestrial origin that burn up as they pass through the atmosphere). The cycle of chemical reactions leading to the emission of the yellow line was demonstrated by Sydney Chapman in 1939. Similarly, the detection of spectral signatures corresponding to transitions between different energy states of the nitrogen atom $N(^2P)$, $N(^2D)$, and $N(^2S)$ showed that the nitrogen molecule N_2, the most abundant chemical species in the lower layers of the atmosphere, is dissociated into nitrogen atoms at high altitudes. These atoms are a source of the nitrogen oxide NO. The presence of the latter is confirmed by the observation of spectral bands corresponding to radiative transitions between different energetic states of the molecule. In 1939, Lars Vegard detected emissions from the hydrogen atom H in the spectrum of the aurora borealis.

An important 1948 study at the Yerkes Observatory in Wisconsin helped to better characterize chemical processes in the upper atmosphere. While working on his Ph.D. at the University of California at Berkeley, the then 25-year-old Aden Baker Meinel (1922-2011) discovered infrared spectral bands in the night

[201] This is the mechanism proposed by Charles Barth of the University of Colorado in 1961 and is written as $O + O + M \rightarrow O_2^* + M$ followed by $O_2^* + O(^3P) \rightarrow O_2 + O(^1S)$ and finally $O(^1S) \rightarrow O(^1D)$ with radiation emission (wavelength 557.7 nm) Here, M represents an atmospheric molecule and O_2^* an oxygen molecule in an excited vibrational state.

sky. He attributed them to the rotational-vibrational spectrum of the radical[202,203]. This was the first evidence that the hydroxyl radical (OH) is present in the upper atmosphere, but the mechanisms that lead to its formation had not yet been elucidated. This discovery was important because it provided the elements needed to understand the dominant chemical mechanisms in the upper atmosphere.

Meinel, who worked for sixty years with his wife, astronomer Marjorie Pettit Meinel (1922-2008), played a major role in the development of astronomy and space exploration in the United States. At the end of World War II, he was sent to Germany to acquire optical and ballistic technology developed by the Nazi regime. At Nordhausen, where the V2 rockets were built, he learned that the Germans had been working on a two-stage rocket capable of reaching the United States. He also helped some German scientists captured by Allied troops reach the United States instead of the Soviet Union. In 1955, he became the first director of the Kitt Peak Observatory in Arizona (1955-1960) and then directed the Steward Observatory at the University of Arizona from 1963 to 1971. He completed his career at the Jet Propulsion Laboratory (JPL) in Pasadena, where he worked with Marjorie on the design of a space telescope. Both researchers were also interested in the possibilities of solar energy.



FIGURE 5.12: Aden and Marjorie Meinel. DR.

[202] A radical (sometimes called a free radical) is a chemical species that possesses one or more "single" (i.e. unpaired) electrons on its outer layer, giving it a high degree of chemical reactivity. This unstable molecule attempts to give up or acquire an electron, thereby transferring its properties to another chemical molecule and initiating a chain of reactions.

[203] The Meinel bands result from the formation of the OH radical in one of the first 9 vibrational levels excited by the reaction between the hydrogen atom and ozone: $H + O_3 \rightarrow OH^{\dagger} (v \leq 9) + O_2$. De-excitation of the radical produces a photon which is emitted according to $OH^{\dagger} \rightarrow OH$ + radiation.

OH EMISSION BANDS IN THE SPECTRUM OF THE NIGHT SKY. I

A. B. MEINEL
Lick Observatory and Yerkes Observatory
Received February 24, 1950

ABSTRACT

High-resolution spectra of the infrared night sky obtained at Yerkes Observatory have shown conclusively that the previously unidentified infrared emissions are due to the rotation-vibration spectrum of *OH*. The agreement between the vibrational spacing, the rotational constants, and the doublet structure of the emissions and the predicted *OH* structure is excellent. The observation of vibrational levels up to $v = 9$ shows that small inaccuracies exist in the currently accepted vibrational constants. A more accurate determination of these constants could be made, despite the low dispersion of the spectrograph. Other bands of this system of *OH* occur in the region of 1 μ and may account for the radiation detected by Stebbins, Whitford, and Swings, which has been attributed to N_2.

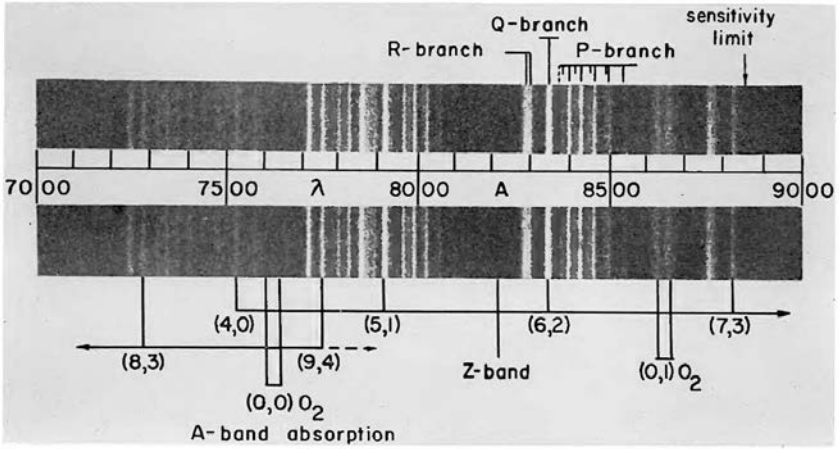


FIGURE 5.13: Top: Summary of Meinel's 1950 article showing the emission bands of the OH radical in the night sky. Bottom: Infrared emission spectrum (700-900 nm) observed with lines corresponding to different transitions in the rotation-vibration spectrum of this radical.

The Oxygen Atom

In 1929, five years after McLennan and Shrum attributed the green line to a radiative transition associated with a metastable state of the oxygen atom, Sydney Chapman, often considered one of the greatest geophysicists of the twentieth century, attempted to interpret the results of his Canadian colleagues. In 1929 he wrote[204]:

> "McLennan's identification of the green auroral line, shown in the spectra both of polar and non-polar aurora, as due to atomic oxygen, proves that oxygen is present in the atomic state at heights of 100 km and above during polar auroral displays, and, in non-polar regions, at all times, in varying measure and at a height which is as yet unknown."

[204] Chapman, S., A theory of upper atmospheric ozone, *Memoirs of the Royal Meteorological Society, 3*(26), 103-125, 1929.

According to Chapman, the formation of the oxygen atom O in the upper atmosphere results from the dissociation of the oxygen molecule O_2 by the energy provided by solar photons, especially ultraviolet radiation. However, these atoms can recombine to form the oxygen molecule[205]. But this recombination becomes less and less likely as the atmospheric pressure decreases, so the concentration of the oxygen atom becomes progressively higher as we rise in the atmosphere above 80 km. Above an altitude which, according to calculations made at the time, would be about 150 km, the concentration of the oxygen atom should become higher than that of the oxygen molecule.

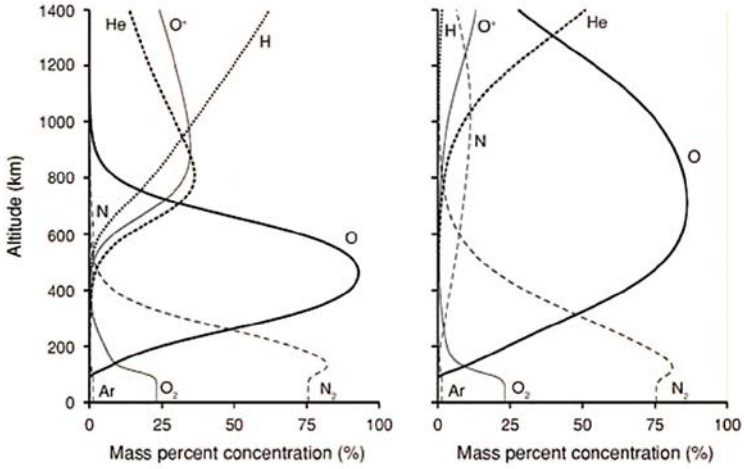


FIGURE 5.14: Vertical distribution of the concentration of several atmospheric compounds as a function of altitude according to the ISSE-00 model by Doornbos (2012). Values are calculated over Delft, (The Netherlands) for July 15 at 6 pm. Left: results for low solar activity. Right values for high solar activity.

However, it wasn't until the advent of rockets after World War II (see Box 5.3) that the vertical distribution of the oxygen atom could be determined experimentally. (see also Boxes 5.3 and 5.4 for details about the development of rockets in Germany during WWII.) Various techniques were used, including photometric observation of the green line produced by the airglow. The concentration of the oxygen atom could also be deduced from the observation of the Meinel infrared bands, taking into account the photochemical processes involved. The first systematic measurements of the oxygen atom from rockets date back to the 1970s. They showed that the oxygen atom, present in very small quantities below 80 km, becomes the most abundant atmospheric constituent above about 250 km. The exact conditions in the thermosphere depend on geophysical conditions and solar activity, which vary considerably with time.

[205] The reactions are as follows: (1) Photodissociation of molecular oxygen: O_2 + UV radiation $\rightarrow$ O + O, and (2) recombination of oxygen atoms to form the oxygen molecule: O + O + M $\rightarrow$ O_2 + M where M represents an atmospheric particle (third body) necessary for conservation of momentum and energy; the third particle can be an atom or a molecule of any kind.

Chapman showed in 1929 that oxygen recombination leads to the formation of the ozone molecule in the stratosphere and mesosphere. We'll return to this subject in more detail in Chapter 6. Here, we will limit ourselves to pointing out the importance in the upper atmosphere of the physicochemical processes initiated by the action of solar radiation on atmospheric molecules. These processes, generated by the influx of energy from extraterrestrial space and responsible for the formation of atoms, chemical radicals, and ions, keep the terrestrial system far from conditions of thermodynamic equilibrium. They form the basis of a new scientific discipline that Chapman, in a letter to the British journal *Nature* in 1946, proposed to call *"aeronomy*" (from the Greek nouns αέρας, aéras, "air" and νόμος, nómos, "law")[206]. The British mathematician and physicist even suggested that the word aeronomy, the science of the air, should replace the old term "meteorology," which he considered too polysyllabic and therefore difficult to pronounce. What Chapman was calling for was a recomposition of the various disciplines concerned with the Earth's atmospheric processes into a single intellectual framework. He wanted to bring together all the components of atmospheric science into a single discipline. And in the journal *Weather*, published in 1946, he didn't hesitate to write an article entitled: *A Plea for the Abolition of "Meteorology*[207]". Obviously, and as one might expect, this proposal was not well received by the meteorologists, and Chapman was therefore forced to limit his ambitions. Today, aeronomy is defined more narrowly as the science of the physical or chemical phenomena that determine the properties of the middle and upper atmosphere of the Earth or, more generally, of the planets. It is the science of atmospheric regions in which dissociation and ionization phenomena play an important role.

Chapman's contribution was not limited to the study of atomic oxygen and ozone in the upper atmosphere. This brilliant mind was interested in a wide range of problems related to the relationship between the Sun and the Earth. His work led to a better understanding of the processes that take place in the magnetosphere and ionosphere; for example, he was interested in magnetic storms associated with solar activity and in the interaction between interplanetary plasma and the Earth's magnetic field. Chapman made important contributions to fundamental questions of gas kinetic theory and thermal diffusion. He was also interested in atmospheric tides in the atmosphere, especially those related to the gravitational attraction of the moon.



FIGURE 5.15: Sydney Chapman. Source: Royal Astronomical Society, London.

Chapman was born in Eccles, near Salford, England, and graduated in engineering from

[206] Chapman, S., Some thoughts on nomenclature. *Nature 157*, 405, 1946.
[207] Chapman, S. A plea for the abolition of "meteorology". *Weather*, *1*, 146-147, 1946.

the University of Manchester. He went on to study mathematics at Cambridge University before being hired as chief assistant at the Royal Observatory in Greenwich. He was also a committed pacifist. At the outbreak of World War I, he offered to become an ambulance driver on the French front, but his application was rejected precisely because of his conscientious objector status. He continued his research in Britain, becoming a lecturer in mathematics at Cambridge University, where he was a fellow of Trinity College from 1914 to 1919. In 1919 he was elected a Fellow of the Royal Society. He continued his career at Manchester University from 1919 to 1924, then joined Imperial College London, where he worked until the outbreak of hostilities in 1940. Deeply concerned by the rise of Nazism and Fascism in Europe, Chapman abandoned his pacifist sentiments to contribute to the defense of his country during World War II. At the War Office, he participated in operational research in support of the war effort. In 1946 he was appointed Professor of Natural Philosophy at Oxford University. It was during this time that he attempted to rally the international scientific community around the concept of aeronomy[208]. After his retirement in 1953, he divided his time between the Institute of Geophysics at the University of Alaska in Fairbanks and the High-Altitude Observatory (HAO) in Boulder, Colorado. At a time when many voices were raised to denounce the dangers of human activities disturbing the atmospheric equilibrium, Chapman preferred to concentrate his intellectual activities on the fundamental study of the processes that determine the dynamic state of the atmosphere. Interestingly, in 1934, he proposed to artificially generate a hole in the ozone layer that would allow astronomers to better study the universe. He died of a heart attack in Boulder in June 1970.

In addition to the esteem in which he was held by his peers, and in addition to his extraordinary scientific productivity, having published more than 400 scientific papers, Chapman had an endearing personality; his colleague Syun-Ichi Akasofu of the University of Alaska attributed many qualities to him: competence, benevolence, humility, integrity, simplicity, courtesy, and courage.

Box 5.3. The First Rocket Launches into the Atmosphere

During World War II, the Germans succeeded in developing a rocket capable of carrying a one-ton payload to an altitude of over 100 kilometers. This was the V-2 rocket, used by the Nazi regime as a deadly weapon to bomb London, Holland, Belgium and northern France. The first rockets were built at the *Peenemünde* center and launched at enemy targets from this facility on the Baltic Sea. German scientists wanted to use the rocket to explore the upper atmosphere. Erich Regener, for example, built an instrument to measure the vertical distribution of ozone at unprecedented altitudes. This plan was not realized, however, because rockets were needed to fuel the war effort. A single test launch was conducted from Peenemünde, and the rocket reached an altitude of 172 km.

[208] The official definition of the term "aeronomy" was introduced at the General Assembly of the International Association of Geodesy and Geophysics, held in Rome in 1954.

A deadly Royal Air Force bombing raid destroyed part of the *Peenemünde* plant, and in August 1943, rocket production was moved to the underground *Mittelwerk* factory in Nordhausen, a town in Thuringia near the Harz Mountains in central Germany. As at Peenemünde, the Nordhausen plant employed a large number of prisoners of war, this time from the nearby Dora concentration camp. In fact, sixty thousand foreign prisoners were forced to help build the weapons of war in Germany.

As the Allies occupied more and more of Germany, and after intense bombing by the British Air Force, American troops were the first to occupy the Nordhausen area on April 11, 1945. This area was handed over to the Red Army on July 2, 1945, and became part of the German Democratic Republic (GDR) after the war. However, the Soviets were unable to gain access to the V-2 rockets captured earlier by American troops commanded by Major William Bromley; they found only a few spare parts produced at the Mittelwerk factory. Over 100 abandoned rockets were sent to the United States. A 300-car train loaded with the booty arrived in Las Cruces, near the *White Sands* military base in southern New Mexico, in July 1945. The V-2 rockets were converted to meet the needs of American space exploration.

In 1946, as part of Operation *Osoaviakhim*, several thousand scientists, engineers, and technicians were deported from the Soviet-occupied zone of Germany to the USSR, where they contributed to the development of ballistic missiles in the Soviet Union. They were held in the USSR for between 8 and 12 years, and all had returned to Germany by 1958. On the American side, about 1,600 Germans, including talented specialists such as Wernher von Braun (1912-1977) and Arthur Rudolph (1906-1996), were exfiltrated in a secret intelligence program called *Paperclip* (see Box 5.4). von Braun, considered the architect of the German space program, was taken to the United States, where he played a major role in the following years, first in the development of the U.S. Army's space programs and then in NASA's construction of the Saturn V rocket to take Apollo to the moon. This father of space conquest became the director of NASA's Marshall Space Flight Center. As for Rudolph, he became head of the Pershing rocket program and then director of the Saturn V program. In 1996, after retiring from NASA, he was forced to leave the United States and renounce his American citizenship to avoid prosecution for his past activities at the Mittelwerk factory.

Between 1946 and 1952, sixty-seven V-2 rockets were converted and launched from White Sands, New Mexico, but only half of these launches were considered successful. Important information about the solar spectrum, the intensity of cosmic rays, and the vertical distribution of ozone was obtained. The use of rockets at the end of the Second World War, which made it possible to study the upper layers of the atmosphere, revolutionized geophysical sciences, as was the case with the launch of the first satellites in 1957. In fact, the acquisition of the V-2 rockets allowed the Americans to become familiar with space technology, to build more compact instruments, and to develop their own rockets for probing the atmosphere. When the V-2s were not available anymore, and given the high cost of assembling them, other sounding

rockets were built in the U.S., notably the *Aerobee*, of which more than 1,000 were launched between 1947 and 1985, making it possible to collect vast amounts of data of great use to a variety of scientific disciplines.

In France, scientists also thought about converting V-2 rockets and using them to explore the upper atmosphere. The military set up a ballistics and aerodynamics research laboratory in the small Normandy town of Vernon, on the banks of the Seine, which employed one hundred and twenty-three German engineers who had been taken over by France after the armistice. These specialists enabled their French colleagues to acquire the knowledge needed to implement the techniques developed at Peenemünde. From 1950, various versions of a rocket called *Véronique* (a contraction of the words "Vernon-electronique") were built. Launched from bases at Hammaguir in the Algerian Sahara, these rockets enabled Etienne Vassy (1905-1969), professor at the University of Paris, and Jacques-Émile Blamont (1926-2020), director of the CNRS Aeronomy Department, to study the dynamic properties of the upper layers of the atmosphere. The scientists studied the dynamics of the atmosphere above 90 km by observing from the ground the dispersion of clouds of metallic vapors (sodium, lithium, potassium) released by the rocket at high altitude. Blamont, who was the first scientific and technical director of the Centre national d'études spatiales (CNES), played a decisive role in shaping the French space program.



FIGURE 5.16: V-2 rocket launched from White-Sands AFB by the Naval Research Laboratory to measure the ultraviolet absorption of solar radiation and the vertical distribution of ozone. NASA.



FIGURE 5.17: Recovery in the desert of New Mexico of the instruments installed on board V2 rocket number 54, launched by the US Naval Research Laboratory (NRL) from White-Sands Air Force Base on January 18, 1951 to make measurements in the upper atmosphere. Richard Tousey, NRL.

Box 5.4. Wernher Magnus Maximilian, Freiherr von Braun: from Germany to the USA

In 1930, the engineer Wernher von Braun, from the small town of Wirsitz in the Kingdom of Prussia (now in Poland), met the Swiss aeronaut Auguste Piccard, who, with his assistant Paul Kipfer, had been the first to ascend to the stratosphere in a balloon. von Braun told him that his dream was to make a trip to the moon. Piccard, impressed by the young man's enthusiasm, encouraged him to put his idea into practice. The German engineer would devote his life to the design of rockets, a military vector whose construction was not prohibited by the Treaty of Versailles after the First World War.

von Braun was employed at the Peenemünde military rocket center along the Baltic Sea, where he became technical director. After joining the Nazi Party in 1937 and joining the *Schutzstaffel (SS)* at the urging of Heinrich Himmler (1900-1945), he developed the Vergeltungswaffen (V-1 and V-2), the spacecraft

advocated by Nazi propaganda minister Joseph Goebbels (1897-1945) to aid Germany's war effort. von Braun's relations with the Nazi regime were tumultuous: at a private dinner in 1943, the engineer confided to a young dentist spying for the SS that he had doubts about the outcome of the war. He was arrested by the Gestapo but released a few days later after the intervention of War Minister Albert Speer (1905-1981). This allowed the V-2 Program to continue.

After the Allied bombing of the Peenemünde plant on August 17 and 18, 1943, the V-2 production line was moved to an underground "Mittelwerk" assembly plant near Nordhausen, Thuringia. Prisoners from the Dora concentration camp (part of the Buchenwald concentration camp) were forced to help produce the rockets.

In early 1945, Soviet troops closed in on Peenemünde, and von Braun and 500 of his employees left the site, taking with them all the technical documents relating to the production of the V-2. These were buried in an iron mine near the town of Goslar in the Harz Mountains, not far from the city of Göttingen. But as Allied troops advanced, and to prevent the rocket specialists from falling into enemy hands, SS General Hans Kammler (1901-1945), in charge of the V-2 project, decided in April 1945 to move von Braun and 450 of his staff to the small Bavarian Alpine town of Oberammergau. But von Braun convinced Kammler that the safest way to protect his team from bombing was to scatter them in nearby villages. This would also allow the group to escape the vigilance of the SS.

After learning that Hitler had given the order to "gas" all engineers and technicians involved in the construction of the V-2 if they were in danger of being captured by Allied forces, von Braun decided, unbeknownst to the SS guards, to commandeer a train and flee with his men to nearby Austria. On May 2, 1945, they arrived in the small town of Reutte in the Austrian Tyrol, which had already been liberated by American troops. Here, Wernher's brother, Magnus von Braun, riding his bicycle, approached an American soldier and said in broken English: "My name is Magnus von Braun. My brother is the inventor of the V-2 rocket. We want to surrender". The American soldier, Fred Schneikert (1910-1985), replied, "I think you're crazy, but we'll investigate". The German scientists were arrested and interrogated. On May 15, 1945, American counterintelligence officers, accompanied by von Braun, went to Goslar and Nordhausen to recover 14 tons of technical documents buried in the mine and to evacuate the engineers and technicians who had remained at the V-2 assembly plant in Nordhausen. The operation was completed two days before Soviet troops took possession of that part of Germany.

On June 20, 1945, the U.S. government decided to expatriate German engineers to the U.S., where they were employed by the U.S. Army Ordnance Corps. The V-2 rockets were sent to the U.S. von Braun first worked in Texas. In 1950, he was transferred to Huntsville, Alabama, where he pursued a brilliant career in the service of NASA.



FIGURE 5.18: German rocket engineers and specialists surrender to American troops (44th Infantry Division) in the village of Reutte, Austrian Tyrol, on May 2, 1945. In the photo from left to right (starting with the seventh person) are Magnus Freiherr von Braun (1919-2003) (Wernher's brother), Wehrmacht Major General Walter Dornberger (1895-1980), director of the V-2 test laboratory, Lieutenant Colonel Herbert Axter (1899-1991), a lawyer from Peenemünde, Wernher von Braun, then 33 years old (injured in a car accident a few weeks earlier), and engineers Hans Lindenberg (1904-1946) and Bernhard Tessmann (1912-1998). They were surrounded by the American military.

Water Vapor and Hydrogen Compounds

In 1949, David Bates (1916-1994) and Marcel Nicolet (1912-1996) met by chance in Pasadena, California, while visiting the California Institute of Technology and the Naval Ordnance Test Station. A specialist in the physics of molecular collisions and atmospheric photochemical processes, Sir David Bates was born in Omagh, Northern Ireland. His family moved to Belfast in 1925, when he was nine years old. It was here that Bates continued his education. In 1934, he enrolled at Queen's University Belfast. It was at his alma mater that he became a professor. Here, he applied the concepts of quantum mechanics and molecular physics to describe the processes taking place in the upper atmosphere. In 1955, this brilliant specialist in theoretical physics and chemistry became a Fellow of the Royal Society in London, and then of several foreign academies (Ireland, USA, Belgium). In Belfast, however, tensions between Catholics and Protestants reached unbearable levels. The prevailing sectarianism led to violent clashes and frequent attacks, often organized by paramilitary groups patrolling the city's

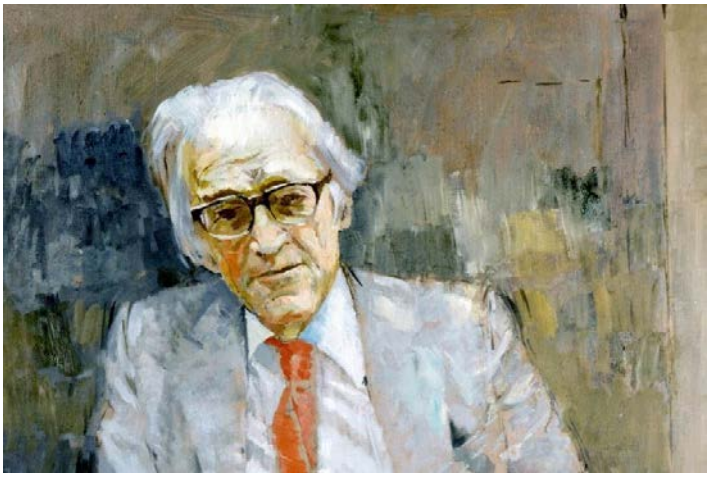


FIGURE 5.19: Portrait of Sir David Bates. © DR.

streets. Bates advocated peace and reconciliation and sought to heal the divisions between citizens by founding a political party in 1970, the Alliance Party of Northern Ireland, of which he was deputy leader for over twenty years.

Baron Marcel Nicolet graduated from the University of Liege in Belgium. There, he worked on the spectra of certain stars and was interested in the effects of solar radiation on the Earth's atmosphere. In 1935, he joined the Royal Meteorological Institute in Uccle, near Brussels, and set out to understand the processes leading to the formation of the ionized layers of the Earth's upper atmosphere. A specialist in the interactions between the Sun and the Earth's atmosphere, he was a member of the Académie Royale de Belgique and the Academies of Sciences of Paris and the United States Academy of Sciences and a frequent guest professor at Pennsylvania State University. In 1964, he founded the Belgian Institute for Space Aeronomy (now the Royal Institute for Space Aeronomy) in Uccle and became its first director.



FIGURE 5.20: Baron Marcel Nicolet.

In Pasadena (California) in 1949, the two researchers had just learned of Aden Meinel's work on infrared emissions from the OH radical and were trying to interpret these measurements. If OH exists at an altitude of 80 to 100 km, what are the mechanisms responsible for its formation? And how does it affect atomic oxygen and ozone?

Bates and Nicolet showed that OH radical formation results from the photodissociation of water vapor by ultraviolet solar radiation. For the energy of the photons to be sufficient to break up the water molecule, the wavelength of the radiation must

be less than 240 nanometers. In reality, the radiation most capable of dissociating the molecule does not penetrate the atmosphere to any significant extent below 75 km, because it is strongly absorbed by molecular oxygen at higher altitudes. In most cases, the dissociation of H_2O results in the formation of an OH radical and a hydrogen atom H, which then reacts with an ozone molecule to form OH in an excited vibrational state[209]. The radical then relaxes to a less energetic vibrational state, producing spontaneous radiative emission. This explains the existence of the Meinel bands that contribute to airglow.

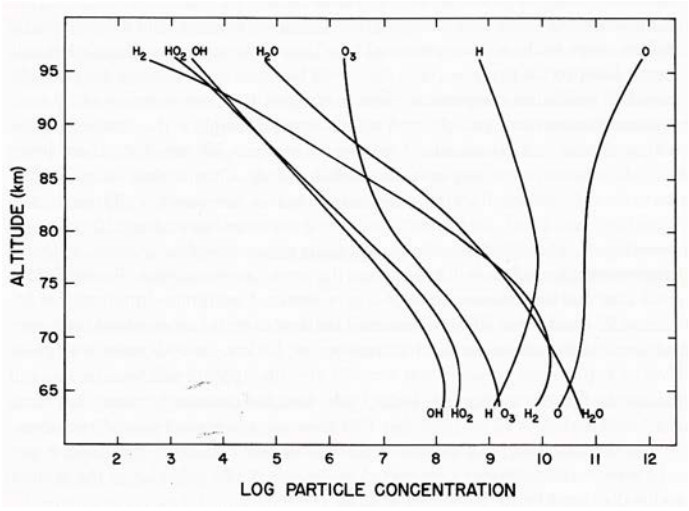


FIGURE 5.21: Average vertical distribution of oxygen and hydrogen constituents in the mesosphere as determined by Bates and Nicolet in 1950, based on their photochemical theory. Source: Bates and Nicolet, The photochemistry of atmospheric water vapor, *Journal of Geophysical Research*, 55, 301-327, 1950.

Bates and Nicolet then set out to determine the relationships between hydrogen compounds (H and OH) and oxygen compounds (O and O_3) that Chapman had studied twenty years earlier. They showed that the hydrogen atom and the hydroxyl radical react with oxygen compounds, providing the first mechanism for the destruction of ozone and atomic oxygen[210]. The proposed

[209] The dominant reaction is $H_2O + hv \rightarrow H + OH$. The hydrogen atom reacts with ozone according to $H + O_3 \rightarrow OH\ (v<9) + O_2$ to form the OH radical in an excited state. In this expression, v represents the quantum number characterizing the vibrational level of the OH radical. The excited OH radical can lose its energy through spontaneous radiative emission, with a change in vibrational level that can range from 1 to 9. The spectrum of this emission was observed by Meinel.

[210] Examples are the following reactions: $H + O_3 \rightarrow OH + O_2$ followed by $OH + O \rightarrow H + O_2$. The combined effect of these two processes, $O_3 + O \rightarrow 2\ O_2$ corresponds to the direct Chapman reaction, but with an accelerated rate of destruction of ozone and atomic oxygen. Another mechanism leading to a similar destruction process is given by the following sequence: $OH + O \rightarrow H + O_2$ followed by $H + O_2 \rightarrow HO_2$ and $HO_2 + O_3 \rightarrow OH + 2\ O_2$.

mechanism is effective because it is a *catalytic cycle*. In other words, each time an oxygen atom and an ozone molecule are destroyed, the hydrogenated compounds are reconstituted and can initiate a new cycle of O and O_3 destruction. The cycle is repeated many times, so that in *the end*, the hydrogenated compounds, while in very small concentration, are very effective at destroying the ozone molecule and the oxygen atom. At an altitude of 80 km, their action reduces the atmospheric concentration of ozone and atomic oxygen by a factor of one hundred. We will return to this topic in Chapter 6.

The International Geophysical Year

An important event was to change the course of atmospheric research activities forever. It took place during a dinner party on April 5, 1950, hosted by James Van Allen and his wife Abigail at their home in Silver Spring, Maryland, and attended by a number of renowned geophysicists, Lloyd Viel Berkner (1905-1967), Sydney Chapman, Siegfried Fred Singer (1924-2020), Ernest Harry Vestine (1906-1968), Merle Tuve (1901-1982) and a specialist in international relations, J. Wallace Joyce (1907-1971). After enjoying an excellent chocolate cake prepared by Abigail Van Allen, Berkner put forward an idea: to organize an International Geophysical Year (IGY), which would be a repeat of the Polar Years of 1882-1883 and 1932-1933. He explained:

> "After dinner, while we were all sipping brandy in the living room, Berkner turned to Chapman and said, 'Sydney, don't you think it's time for another International Polar Year?'."

Chapman immediately embraced the suggestion, noting that he had been thinking along the same lines. The discussion then turned to the scope of the enterprise and practical considerations of how to contact leaders in a wide range of international organizations to enlist their support. The year 1957-58, the 25th anniversary of the second polar year, and the expected maximum solar activity was chosen.

The proposal was enthusiastically received by the evening's participants. A few days later, it was presented to the broader academic community. Scientists were immediately convinced by the idea, but it faced a major difficulty: the Cold War between East and West. Nevertheless, it was adopted in 1951 by several international organizations, including the International Union of Geodesy and Geophysics (IUGG) and the International Council of Scientific Unions (ICSU). It was implemented under the guidance of a Special Committee for the International Geophysical Year based in Brussels, Belgium.

It was because he combined all these scientific and human qualities that Sydney Chapman was chosen to preside over this great scientific undertaking, sometimes called the Olympiad of Science. The program, coordinated by IGY Secretary General Marcel Nicolet, ran from July 1957 to December 1958. International tensions between the Eastern and Western blocs, especially after the Berlin Blockade (1948-1949) and the Korean War (1950-1953), as well as the specter of global nuclear conflict, did not make the task of the



FIGURE 5.22: The home of James and Abigail Van Allen, 1105 Meurilee Lane in Silver Spring, Maryland, where the idea of organizing an International Geophysical Year was presented and discussed at a private dinner held on the occasion of Sydney Chapman's visit and attended by a group of geophysicists. Source: *Physics Today* **60**, 7, 38 (2007).

program's leaders easy. However, scientists hoped that the implementation of a global project involving the exchange of ideas and data would reduce geopolitical tensions. The first step was to convince the U.S. State Department to allow the USA to participate, which Lloyd Berkner skillfully did. However, it wasn't until 1954 (after Joseph Stalin's death in 1953) that the Soviet Union accepted the invitation to join the IGY. The People's Republic of China joined in 1955 but withdrew a few months later to protest the presence of scientists from Taiwan.

Despite the political difficulties that arose, the International Geophysical Year ended the delicate period when exchanges between scientists from the Western and Eastern blocs were not permitted. However, scientific cooperation between researchers from the two blocs remained tentative due to political constraints and military interests on both sides of the Iron Curtain. Fear of espionage and the defection of scientists between the blocs did not encourage the desired exchanges. At the same time, the military on both sides saw a real opportunity in the IGY: to gain a better understanding of the processes in the upper atmosphere that could slow the trajectory of ballistic missiles and those that determine the transmission of radio waves.

Sixty-seven nations decided to join the IGY and contribute to the study of solar-terrestrial relations, including solar activity, cosmic rays, the upper atmosphere, geomagnetism, the ionosphere, the aurora and airglow, and more generally, meteorology, oceanography, glaciology, gravimetry, and seismology. Antarctica was both a territory to be explored and a geopolitical challenge.

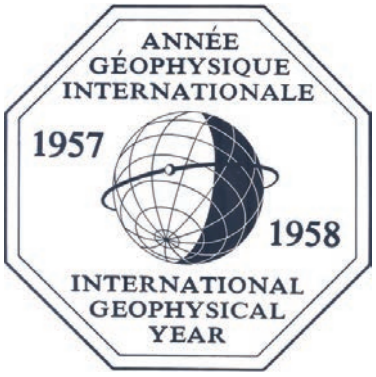


FIGURE 5.23: International Geophysical Year logo.

On October 4, 1957, at the beginning of the International Geophysical Year, an unexpected event occurred. The Soviets, without informing those in charge of the program, launched the first artificial satellite, *Sputnik-1*, into orbit. This came as a complete surprise to the Americans, who were understandably irritated. As Christy Collis and Klaus Dodds write in the *Journal of Historical Geography*[211]:

> "If the post-war period was largely defined by Cold War competition and decolonization in the Global South, the IGY demonstrated that the Earth's surface was also far from settled in terms of political jurisdiction. The IGY ushered into existence a new phase of exploration and colonization of apparently remote spaces such as Antarctica and outer space and yet it also contributed to a conceptual shift in the ways in which the Earth and beyond was imagined, understood and managed. As Sputnik I orbited the Earth in October 1957, the international community's attention shifted towards the heavens. The *New York Times* headline 'Soviet fires earth satellite into space: it is circling the globe at 18,000 mph; sphere tracked in four crossings of the United States' conveyed some of the challenges facing the post-war global political order – the legal ownership and political management of outer space."

A few months later, on January 31, 1958, the USA launched Explorer-1, a small 8 kg satellite carrying a small Geiger-Müller counter to measure cosmic radiation. However, no measurements were taken because the Geiger tube was apparently saturated. New measurements taken during the Explorer 3 mission showed that the satellites had passed through a region of high density of high-energy particles. This led to the discovery of the Van Allen belts surrounding the Earth. These belts extend from about 600 to 58,000 km above the Earth's surface, where charged particles (electrons and protons) are trapped by the Earth's magnetic field. This is believed to be the first scientific discovery made from an artificial satellite.

[211] Collis, C., Dodds, K., Assault on the unknown: the historical and political geographies of the International Geophysical Year (1957-8). *Journal of Historical Geography, 34*, 555-573, 2008.

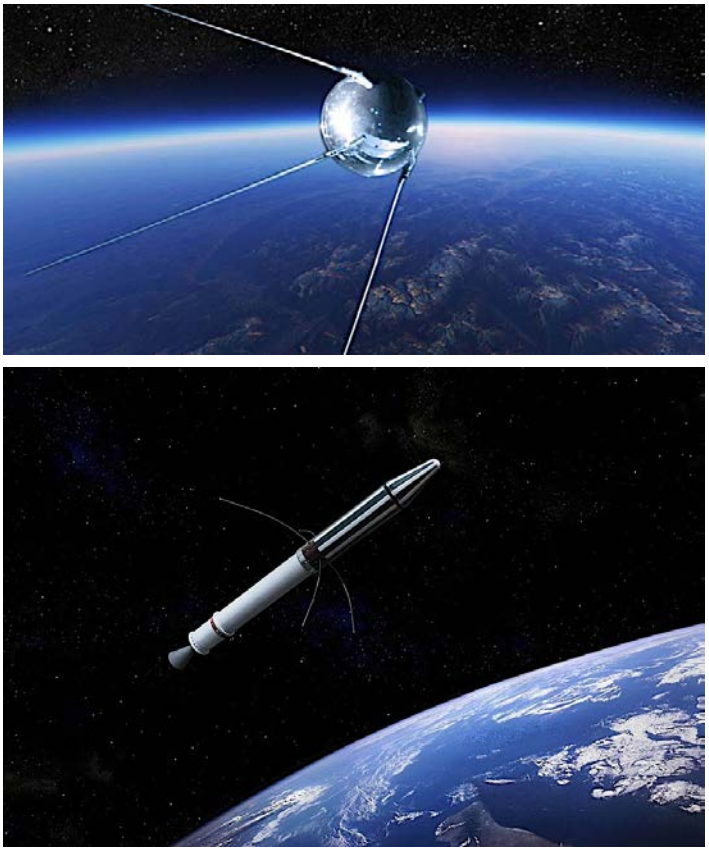


FIGURE 5.24: The first artificial satellite: Sputnik-1, launched by the Soviet Union in 1957, and Explorer-1, launched by the United States in 1958.

During the International Geophysical Year, other initiatives were taken; a particular effort was made in Antarctica, where observation stations were set up by several countries. Antarctic research is eminently political, with several nations vying for territory to conduct their own research and perhaps gain a dominant position in the Southern Hemisphere. For example, the two closest countries, Argentina and Chile, believed that distant countries such as Great Britain, France, and Norway had no right to acquire territory on this continent. Against this backdrop, where geopolitics and science met, and where the powers of the northern hemisphere played a decisive role, especially under the impetus of the International Geophysical Year, an international Antarctic Treaty was adopted in 1959. It stipulates:

> "Antarctica shall be used for peaceful purposes only. All measures of a military nature, such as the establishment of military bases and fortifications, the execution of military maneuvers and the testing of any type of weapon, are prohibited.

> Freedom of scientific research in Antarctica and cooperation to this end, as applied during the International Geophysical Year, shall continue, subject to the provisions of the present Treaty."

In the years that followed, the stations, which became permanent laboratories, provided important information on the disturbances affecting this polar region, on the long-term evolution of the climate, and more recently, on the formation of a "hole" in the ozone layer over Antarctica. These included the British Halley Base, the American Amundsen-Scott Base, the Soviet Vostok Base, and the Japanese Syowa Base.



FIGURE 5.25: Sydney Chapman surrounded by members of the Special Committee of the International Geophysical Year with, from left to right, Jean Coulomb, Marcel Nicolet, Sydney Chapman, Lloyd V. Berkner, and Vladimir V. Belousov at a meeting in 1959. Source: Syun-Ichi Akasofu.

The Thermosphere, the Hydrogen Layer, and the Helium Belt

In the 1960s, the conquest of space was a major political issue, but it also played a central role in research projects. Satellites made it possible for the first time to study the structure and chemical composition of the thermosphere, the layer of the atmosphere above 100 km. This layer has two characteristics that distinguish it from regions at lower altitudes. First, the temperature is very high (about 750 Kelvin[212]) and rises sharply during periods of high solar

[212] Kelvin is the unit of temperature defined as Celsius plus 273. Absolute zero (zero Kelvin) corresponds to a temperature of −273 degrees Celsius.

activity, reaching 2000 K. Second, turbulent mixing of the thermosphere and atmosphere is a major source of heat. Third, the large-scale turbulence that creates mixing conditions below 80 km altitude and keeps the relative content of the major gases uniform (79% for nitrogen and 21% for oxygen) no longer occurs at high altitudes, where air density becomes extremely low. Thus, in the thermosphere, where collisions between atoms and molecules are rare, air particles are mainly subject to gravity, so heavier chemical species diffuse downward while lighter species diffuse upward. In the upper layers of the atmosphere, these lighter species become the most abundant compounds. This is known as *diffusive separation* between compounds of different masses. As early as 1920, Chapman, working at Cambridge with the astrophysicist Edward Arthur Milne (1896-1950), distinguished between two atmospheric regions with very different dynamic properties. One, the troposphere, is subject to intense mass and energy exchange due to turbulence and convection, while the second, which Chapman erroneously placed above 20 km (rather than above 100 km) and whose temperature is constant with altitude, is not subject to the mass exchange generated by turbulence. It is in this second layer that the diffusive separation of chemical compounds according to their respective atomic/molecular masses takes place.

Which low-atomic-mass constituents would become the majority compounds in the upper thermosphere? The first idea that comes to mind is atomic hydrogen. Chapman and Milne considered this possibility but found that free hydrogen is very scarce near the ground and that the hydrogen atom would probably have to combine very rapidly with oxygen before it could diffuse into the stratosphere and reach the highest layers of the atmosphere. Chapman and Milne then suggested the presence at high altitudes of another light gas: helium, which is inert and therefore not destroyed like hydrogen. This proposal was challenged by Sir James Hopwood Jeans (1877-1946). This brilliant mathematician, astronomer, and specialist in theoretical physics wrote in his book *The Dynamical Theory of Gases* that hydrogen should become the dominant atmospheric constituent above 75 km, despite its low concentration at ground level. Jeans went on to establish the mathematical formalism for calculating the amount of hydrogen that could be released from the Earth into interplanetary space, free of the forces of gravity. The debate between Jeans and his colleagues Chapman and Milne remained open for three decades; it wasn't until the 1950s that the dilemma was resolved.

Despite the inaccuracies that characterize it, the work of Chapman and Milne, published in 1920, is that of two pioneers of atmospheric research. It demonstrated for the first time the existence of two specific dynamic regimes, each applicable to two regions of the atmosphere. Today we know that the separation between these two layers occurs at about 100 km and not, as Chapman and Milne assumed, at 20 km; these layers are known as the *homosphere*, the region in which mixing conditions dominate (comprising the troposphere, stratosphere, and mesosphere), and the *heterosphere,* the region (essentially corresponding to the thermosphere) dominated by molecular diffusion, which leads to a vertical separation of chemical compounds according to their respective molecular masses.

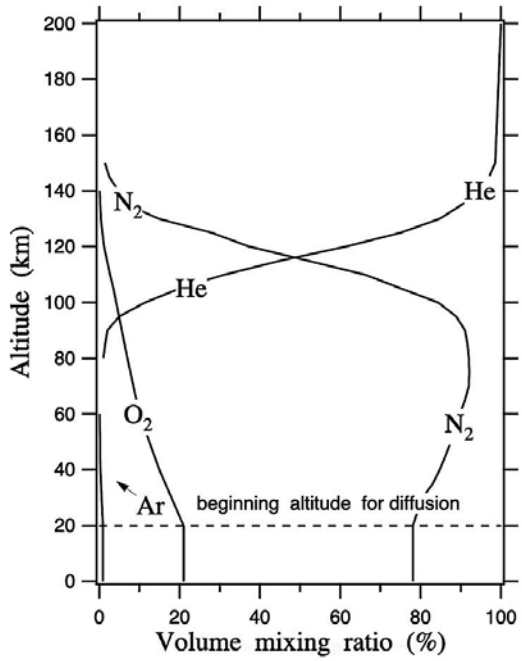


FIGURE 5.26: Vertical distribution of mole fractions of atmospheric constituents imagined by Chapman and Milne in 1920, based on data available at that time. The two authors believed that the major atmospheric constituents, such as nitrogen and oxygen, are mixed by turbulence and convection in the layer below 20 km altitude, and that molecular diffusion produces an altitude-dependent separation of chemical compounds according to their mass. They concluded that helium becomes the most abundant constituent in the upper atmosphere. This initial representation of the composition of the upper atmosphere was later modified.

In the late 1950s and 1960s, artificial satellites provided new information to better characterize the structure and composition of the upper atmosphere and to test the hypotheses of the three Trinity College Oxford affiliates, Chapman, Milne, and Jeans. Two other leading scientists were using the measurement of satellite orbital variations to infer air density in the thermosphere. One was the Italian astronomer Luigi Guiseppe Jacchia (1910-1996), and the other was the British physicist Desmond George King-Hele (1927-2019).

Jacchia studied at the University of Bologna before becoming an assistant at the city's astronomical observatory, where he worked on variable stars and solar physics. Following the racial laws enacted by Mussolini's Fascist government in 1938, which targeted Jewish scientists and intellectuals, he decided to emigrate to the United States a year later. There, he joined the Harvard College Observatory (Massachusetts), but his career was interrupted by the Second World War. Jacchia's excellent linguistic skills, speaking more than a dozen languages, led him to join the US Office of War Information, where he contributed to the war effort. From 1956 to 1980, he worked at the Smithsonian

Institution's Astrophysical Observatory, where he turned his research to geophysics and atmospheric physics. His work focused on determining the density of the upper atmosphere from its effects on the motion of artificial satellites. His empirical models of air density in the thermosphere are of particular value to those planning space missions and wishing to determine the drag on spacecraft motion.

King-Hele, who studied mathematics at Trinity College, Cambridge, also sought to use satellites to determine the vertical structure of the thermosphere. He established a mathematical formalism that allowed him to estimate the effect of air resistance on satellite motion, particularly in the perigee region of their orbits[213] and thus derive the density of air at these altitudes. His analyses included the orbital variations of the Soviet satellites Sputnik 1, 2, and 3 and the American satellites Explorer I, Vanguard I, and Explorer IV. Elected a Fellow of the Royal Society in 1966, King-Hele, who was Deputy Director of Scientific Research at the Royal Aircraft Establishment in Farnborough, was also a talented writer. In addition to his scientific books, he published several collections of poetry and several biographical works. One of these, published in 1960, is dedicated to the Romantic poet Percy Bysshe Shelley (1792-1822), whom he admired. Another was about the physician Erasmus Darwin (1731-1802), grandfather of the famous Charles Darwin, who is said to have influenced the English Romantic poets. Finally, his book *The End of the Twentieth* Century, written in 1970, attempts to predict how the world will evolve under the impact of technological development in the face of increasing pollution of the planet.

The variation of air density with altitude derived by Jacchia and King-Hele is often expressed by an equivalent quantity called the *scale height* (see Chapter 2). Its value is about 7 to 8 km below 80 km altitude, but increases rapidly with height above this level, reaching values of more than 500 km at about 1000 km altitude. Such an increase can only be explained if the composition of the atmosphere changes with altitude in favor of lighter compounds. Only the presence of atomic hydrogen can explain orbital variations and specifically the observed deceleration of artificial satellites. An important conclusion to be drawn from the work of the two Italian and British researchers is that hydrogen is the most abundant chemical species above about 1000 km. Does this mean that Chapman and Milne's hypothesis presented in the second decade of the twentieth century was wrong? In fact, it was correct to assume that free hydrogen, which is present in small amounts near the Earth's surface, combines rapidly with oxygen and therefore cannot be transported to high altitudes. However, these two scientists could not have known in 1920 that the hydrogen atom is produced in the atmosphere above 80 km by the photodissociation of water vapor, as demonstrated by Bates and Nicolet in 1950.

While Jacchia and King-Hele were analyzing the perturbations affecting satellite motion, Nicolet and Gaston Kockarts were calculating the vertical distribution of chemical species in the thermosphere, considering the vertical exchange produced by molecular diffusion and using the information provided by the first space observations. The mathematical basis for the development of such models,

[213] The point in the orbit closest to the Earth.

which took into account the molecular diffusion of chemical species and heat conduction, was based on the kinetic theory of gases by James Maxwell (1831-1879) and Ludwig Boltzmann (1844-1906) and was adapted in 1939 by Sydney Chapman and Thomas George Cowling (1906-1990) to the specific problems of the upper atmosphere[214]. These models clearly showed that the hydrogen atom is the most abundant atmospheric compound above about 1000 km, or at higher altitudes during periods of high solar activity. But what Nicolet and Kockarts' model also showed is the existence of a helium-dominated layer between 700 and 950 km altitude. In 1961, Nicolet claimed that the changes observed in the orbital period of the American satellite Echo-1 around the Earth could only be explained by the presence of this helium belt surrounding our planet. In particular, the analysis of satellite drag by Gerald Maurice Keating (1936-2010) at NASA showed that the density of helium in the thermosphere over the polar regions is about three to four times higher than that observed in summer. Measurements by mass spectrometers on board rockets and satellites confirmed the existence of a winter helium maximum at high latitudes. Recent thermospheric models, such as the one developed by Raymond Roble at the National Center for Atmospheric Research (NCAR), which consider the effects of diffusion and the general circulation of the atmosphere, demonstrate the importance of atmospheric dynamics in addition to the effects of molecular diffusion, which was the only factor considered in Nicolet's early models.

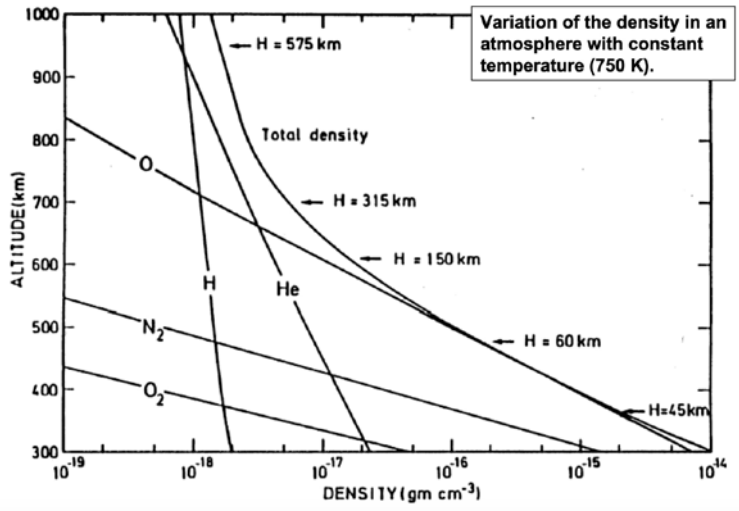


FIGURE 5.27: Vertical distribution of the concentration of atmospheric chemical compounds between 300 and 1000 km altitude during a period of low solar activity (atmospheric temperature 750 K). Note the dominant components: oxygen below 650 km, helium between 650 and 950 km, and hydrogen above 950 km.

[214] Chapman, S., Cowling, T.G., *The mathematical theory of non-uniform gases. An account of kinetic theory of viscosity, thermal conduction and diffusion in gases*, Cambridge University Press, 1939.

Helium was first observed in 1868. A yellow spectral line (587.49 nm) emanating from the Sun's chromosphere was detected at Guntur in India by the French astronomer Pierre Jules César Janssen[215] (1824-1907), who observed the solar eclipse of August 18 of that year through a prism. This spectral signature of helium was first attributed to sodium, which has lines in this region of the spectrum. In the same year, the English astronomer Sir Joseph Norman Lockyer[216] (1836-1920), who also observed this line on October 20, 1868, noticed that its wavelength was close to but different from, that of sodium. He concluded that a previously unknown element had been discovered in the solar atmosphere. Lockyer and the British chemist Sir Edward Frankland (1825-1899) named this element helium, after the Greek name ἥλιος (*helios*, sun). The two papers describing Janssen's and Lockyer's observations arrived at the Académie des Sciences in Paris on the same day, so the discovery of helium in the solar atmosphere was attributed to both astronomers.

Janssen continued his systematic observations of solar radiation, traveling around the world to observe several eclipses between 1870 and 1905. To observe the eclipse of December 22, 1870, in Oran, Algeria, during the Franco-Prussian War, he escaped from the French capital, then besieged by German troops, on December 2, 1870. To accomplish this feat, he boarded a hot-air balloon that took off from Orléans train station at six in the morning and flew over enemy lines. Janssen, accompanied by "Fusilier marin" (Sailor rifleman) Chapelain, took a telescope for his measurements. The balloon landed at Briche-Blanc, near St. Nazaire. Janssen then took the train to Tours, the seat of the provisional French government, to meet the Minister of the Interior and War, Léon Gambetta (1838-1882), who had himself fled Paris by balloon. The astronomer then went to Marseilles, where he embarked for Algeria. However, the mission was a failure: the eclipse could not be seen because the cloud cover was too thick. In 1893, Janssen developed the Mont Blanc Observatory and, despite his physical handicap, climbed the mountain at the age of 69 and spent several days in the observatory.

At the time, no one imagined that helium could exist on Earth. However, in 1881, the Italian physicist Luigi Palmieri (1807-1896) detected this element in the matter ejected from Mount Vesuvius in Italy. In 1885, as mentioned above, Sir William Ramsay isolated helium by processing uranium ore. Ten years later, he suggested that helium was probably released into the atmosphere by outgassing from the Earth's crust and mantle, where it is produced by the radioactive decay of thorium-232 and uranium-288, and 235. Helium, first identified in the extraterrestrial world, is actually present on Earth and in its atmosphere. It is the most abundant compound in a layer over 200 km thick in the thermosphere.

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[215] Jules Janssen, whose youth was disrupted by a serious accident that left him permanently unable to walk, had to interrupt his studies and work as a clerk from the age of 16. In his spare time, he studied mathematics and was admitted to the Sorbonne, where he completed his doctorate in 1860. Eight years later, he was elected a member of the Paris Academy of Sciences and, until his death in 1907, became the first director of the Meudon Astronomical Observatory in 1876.

[216] J. Norman Lockyer is also the founder and first editor of the renowned scientific journal *Nature*.

The Ionosphere

The propagation of electromagnetic waves, highlighted by the work of the Scottish mathematician James Clerk Maxwell (1831-1879), the Dutch physicist Hendrik Antoon Lorentz[217] (1853-1928), and German physicist Heinrich Hertz (1857-1894), led to the discovery of previously unknown properties of the upper atmosphere in the early twentieth century. In 1894, the Italian engineer Marquis Guglielmo Giovanni Maria Marconi (1874-1937) made the first attempt to establish a "wireless" connection between a radio transmitter and a receiver. Early results were encouraging. Marconi's ambition was to compete with the traditional telegraph with a revolutionary system known as the wireless telegraph, or WT. Beginning in 1899, he equipped some modern ocean liners with radio-electric systems to provide passengers with the latest news at sea. It was thanks to such a system that, on April 15, 1912, employees of the *Marconi International Maritime Communication Company* sent out SOS messages aboard the *Titanic*, and a nearby ship, the *Carpathia*, picked up many passengers lost on the ship. This prompted the British Postmaster General to say:

> "Those who have been saved, have been saved through one man, Mr. Marconi and his marvelous invention."

More than fifteen hundred passengers and crew perished in this terrible accident. During World War I, when the luxurious British liner *Lusitania* was sunk by a German submarine off the northern coast of Ireland on May 7, 1915, killing more than a thousand passengers, it was again thanks to radio that rescue services were alerted.

In the early twentieth century, in search of an alternative to cable transmissions across the Atlantic, Marconi attempted to establish a radio link between Europe and the east coast of the Americas. He set up a transmitting station at Poldhu, Cornwall, and went to Signal Hill, near St. John's, Newfoundland, to install a powerful receiver in an old hospital on a hill that had become available after being destroyed by fire a few months earlier. Marconi was looking for a signal from Poldhu - the letter S in Morse code - that he claimed to have heard on December 12, 1901. Many were, and still are, skeptical because the wave propagation conditions for this transmission were far from optimal. The experiment was repeated in February 1902; again, Marconi claimed to have heard the signal from Poldhu while sailing on the SS Philadelphia towards the United States. On December 17, 1902, a radio message crossed the Atlantic for the first time from Glace Bay, Nova Scotia, and on January 18, 1903, Marconi transmitted a message from U.S. President Theodore Roosevelt to King Edward VII of Great Britain.

Marconi now enjoyed a high reputation and became a senator of the Kingdom of Italy in 1914. A few years after World War I, he joined the Fascist movement. Benito Mussolini appointed him president of the Royal Italian Academy in 1930. Earlier, in 1924, he had founded the *Unione Radiofonica Italiana*, the forerunner of Italian radio and television.

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[217] Nobel Prize in Physics (1902).

Marconi's experiments showed that certain long-range radio waves had to be reflected in the atmosphere before they could be sent back to the surface. The American engineer Arthur Edwin Kennelly (1861-1939) and the mathematician and physicist Oliver Heaviside (1850-1925) showed that there must be an electrically conductive layer in the upper atmosphere that allows radio waves to follow the curvature of the Earth instead of propagating in a straight line into interplanetary space. The existence of electric currents had been postulated as early as 1841 by the German mathematician and physicist Carl Friedrich Gauss (1777-1855) and the Scottish physicist and astronomer Balfour Stewart (1828-1887) to explain variations in the Earth's magnetic field. Electric current also means the presence of free electrons moving under the influence of an electric field.

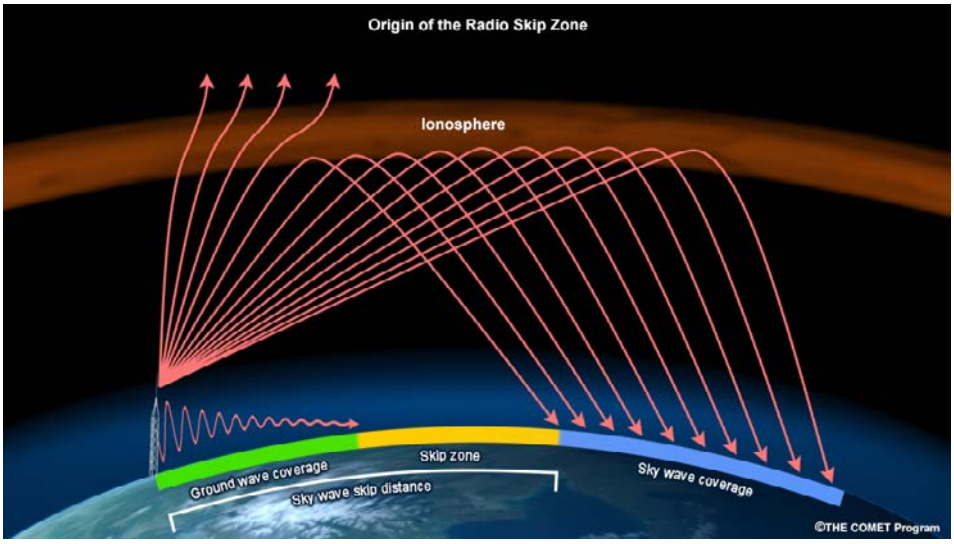


FIGURE 5.28: Radio wave emission, in particular a ground wave that is rapidly attenuated and therefore covers a limited distance. We can also see the trajectory of the waves, which are directed towards the sky and, when the angle of incidence does not exceed a certain value, are reflected by the ionosphere. The waves reach the ground in regions far from the transmitter. Note the existence of a "skip zone", i.e. an intermediate region of silence in which neither the ground wave nor the reflected wave can be picked up.

At the time of Gauss and Stewart, the source of electrical charges (electrons and ions) was unknown. It wasn't until 1903 that J. E. Taylor made an interesting and important suggestion: that electric charges were produced by the action of solar ultraviolet radiation on atmospheric molecules and atoms. In a paper published by the Royal Society, he wrote[218]

> "The following notes refer to effects which appear to have a distinct connection with the so-called 'ionization' of the upper regions of the atmosphere by

[218] Taylor, J.E., "Characteristics of electric Earth-current disturbances, and their origin." Communicated by Sir Oliver Lodge, F.R.S. Received December 16, 1902, -Read January 22, 1903. *Proceedings of the Royal Society of London, 71*, 467-476, 1903.

radiations from the sun, and which have repeatedly attracted my attention during the course of recent experiments in wireless telegraphy for the British Postal Telegraphs.

In the electronic theory of the causes producing aurora borealis, it is assumed that the deflection of the course of the flying ions or electrons towards the poles, due to the earth's magnetic field, a concentration results in those neighborhoods, giving rise to the phenomenon.

The effects classed by telegraph engineers as earth-currents have also, apparently, a direct connection with the ionization of the atmosphere. As is well known, these are at times, particularly when auroral display are in evidence, so strongly pronounced as to interfere more or less with ordinary telegraphic working on earthed circuits."

Taylor proposed that the propagation of radio waves is controlled by solar activity. Photons from the sun, if their energy is high enough, can indeed extract an electron from an atom or molecule. Only the most energetic ultraviolet rays and X-rays provide the energy necessary to ionize neutral constituents such as oxygen (O_2) and nitrogen (N_2) molecules, and oxygen (O), helium (He), and hydrogen (H) atoms. These short-wave incident rays, which are rapidly absorbed by atmospheric compounds, do not penetrate below an altitude of 100 km. Ionized regions are therefore found mainly in the thermosphere.

Without explicitly mentioning it in his article, Taylor introduced a concept that is still relevant today, known as *space weather*. These are random disturbances of short duration (a few hours to a few days) that occur in the upper atmosphere because of irregularities in radiation intensity or in the flow of energetic particles from the Sun. These disturbances directly affect ionization processes and, if intense, can even disrupt data transmission systems or interrupt the distribution of power through high-voltage lines.

Specialists in wireless telegraphy set out to determine the height of the layer reflecting radio waves. This was the case between 1912 and 1914, thanks to the American inventor Lee de Forest (1873-1961) and the engineer Leonard. F. Fuller at the *Federal Telegraph Company* in San Francisco. However the

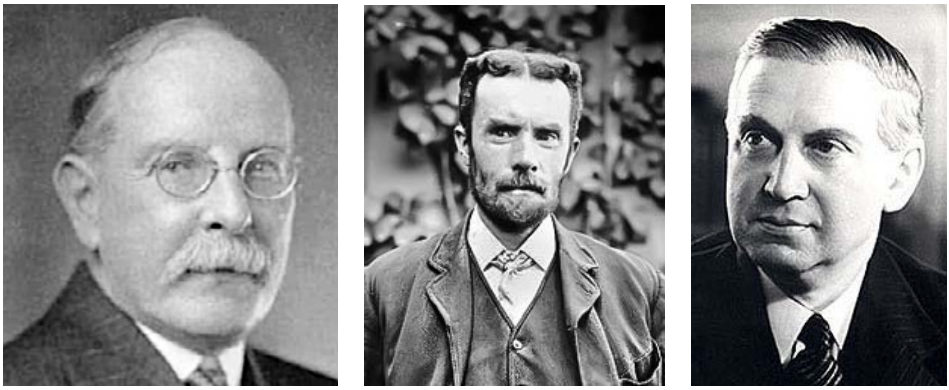


FIGURE 5.29: Three pioneers of ionospheric research. From left to right: Arthur Edwin Kennelly, Oliver Heaviside and Sir Edward Victor Appleton.

measurements that really caught attention were not made until 1924: in the U.S., by the Russian-born physicist Gregory Alfredovich Breit-Schneider (1899-1981) and the geophysicist Merle Anthony Tuve (1901-1982); in the U.K., by the physicist Sir Edward Victor Appleton[219] (1892-1965) and his student, the New Zealand meteorologist and physicist Miles Aylmer Fulton Barnett (1901-1979). Their work clearly showed that the reflective layer of radio waves is found above 100 km altitude.

In 1926, the name *ionosphere* was introduced by Sir Robert Alexander Watson Watt (1892-1973), a Scottish pioneer of radio and radar technology. In a letter to the Secretary of the Radio Research Board dated November 8, 1926 (not published by Nature[220] until 1969[221]), he wrote:

> "We have in quite recent years seen the universal adoption of the term 'stratosphere' in lieu of a previously well-established misnomer 'isothermal layer', and the adoption of the companion term 'troposphere' for the 'convective layer'. The term 'ionosphere', for the region in which the main characteristic is large scale ionization with considerable mean free paths, appears appropriate as an addition to this series."

Watson-Watt thus characterized the layer of the Earth's atmosphere that contains a high concentration of ions and free electrons and is capable of reflecting radio waves. In his early work, Appleton used the letter *E* to designate the electric field of the first layer he was able to identify. Subsequent radio soundings, however, showed that there were several ionized layers at different altitudes, or at least several regions, each characterized by a maximum electron concentration. Appleton then extended his nomenclature by defining the *D*, *E,* and *F regions* of the ionosphere with different letters. A member of the Royal Society, he was awarded the Nobel Prize in Physics in 1947 for his experimental work proving the existence of the ionosphere. Today, we know the characteristics and physicochemical properties of the various layers containing charged particles. The vertical distribution of the concentration of electrons and ions is also well-known (Box 5.5). We know that the concentration of electrically charged particles is a very small fraction of the concentration of neutral particles. The upper atmosphere is therefore considered to be a weakly ionized plasma.

The *D region* of the ionosphere extends from 70 to 90 km above sea level. As Marcel Nicolet demonstrated in 1945, this layer is formed by the ionization of nitrogen oxide (NO) under the action of solar radiation, and more specifically by an intense line in the solar spectrum: the Lyman α line at 121.6 nm. Cosmic rays and X-rays also contribute to the ionization of this layer. The *D region*, which strongly absorbs high-frequency radio waves, disappears rapidly after sunset due to rapid recombination between ions and electrons. During winter, the electron concentration can be abnormally high, resulting in increased absorption of radio

[219] Nobel Prize in Physics (1947).

[220] Gardiner, W., Origin of the term Ionosphere. *Nature, 224*, 1096, 1969.

[221] A file copy of the letter was discovered during building alterations at the Radio and Space Research Station, Slough.

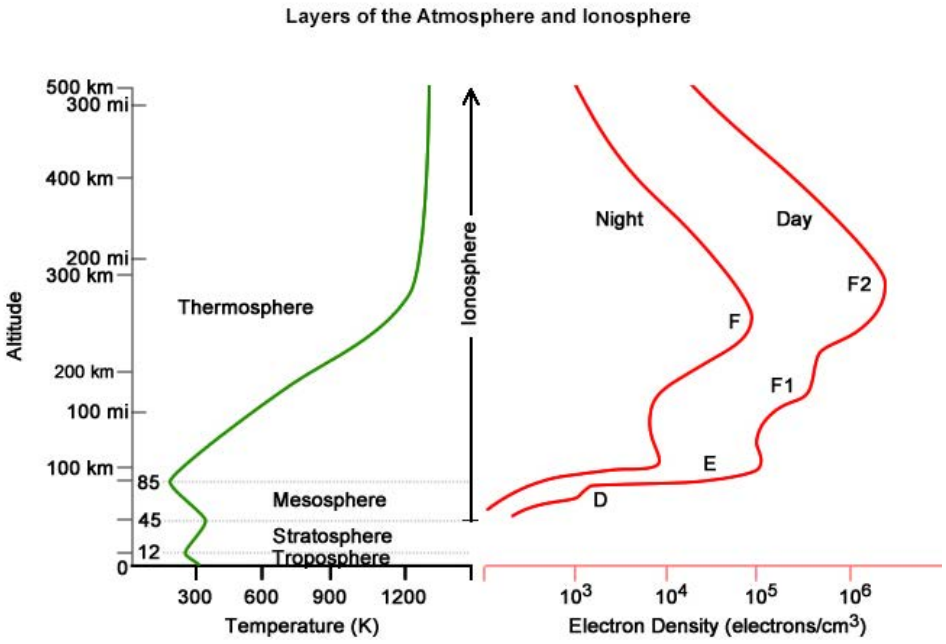


FIGURE 5.30: Left: Vertical temperature distribution from the Earth's surface to 500 km altitude and atmospheric layers defined by the thermal structure of the atmosphere. Right: Ionospheric layers with different regions during day and night.

waves. This winter anomaly is related to the existence of planetary waves that develop in the upper atmosphere during this season.

The *E region* of the ionosphere, originally called the *Kennely-Heaviside layer,* extends from 90 to 150 km. It results mainly from the ionization of molecular oxygen by far ultraviolet and soft X-rays (1 to 10 nm) from the Sun. It reflects waves with frequencies below 10 MHz and attenuates those with higher frequencies. Since the recombination rate of charged particles is relatively fast, the layer disappears around midnight. Sporadically, the electron concentration can increase by several orders of magnitude around 100-110 km altitude. This anomaly, which affects the propagation of electromagnetic waves, is related either to the precipitation of energetic particles at high latitudes or to perturbations in atmospheric dynamics.

The *F region* of the ionosphere, sometimes called the *Appleton-Barnet layer*, extends from 150 to 500 km above the Earth's surface. It is formed by the ionization of the oxygen atom under the influence of extreme ultraviolet radiation (10-100 nm). A distinction is often made between the *F1 layer*, which is present only during the day, and the *F2* layer, which remains at night. It is the latter layer that allows intercontinental shortwave radio communications. This technology is used by amateur radio operators who communicate with each other around the world, mainly at night. Before the advent of satellites, shortwave communications were used extensively by the military.

Box 5.5. Ion Chemistry

The chemical composition of the ionosphere has been studied since the late 1950s, thanks to observations made by rocket-borne mass spectrometers. The principle of these instruments is simple: the air sampled and containing the ions is subjected to a magnetic field created inside the instrument, and the deflection of the ions under the effect of this field depends on the mass of each of the ions. The mass spectrum thus obtained makes it possible to reconstruct the concentration of each type of ion in the sampled air.

The first measurements were made using rockets launched by American military laboratories. For example, Charles Yothers Johnson[222] (1920-2004) of the Naval Research Laboratory (NRL) in Washington showed from measurements taken in 1956 and 1958 over Fort Churchill in northern Canada that the most abundant ions between 100 and 250 km altitude were those with atomic masses of 16, 30, and 32, i.e. O^+, NO^+ and N_2^+. Measurements taken over Florida in 1963 by R. S. Narcisi and A. D. Bailey of the Air Force Cambridge Laboratory indicate that the most abundant ions between 65 and 85 km altitude are those of mass 30, 19, and 37. These are identified as the NO^+ ion and the hydrated protons $H^+(H_2O)$ and $H^+(H_2O)_2$, respectively.

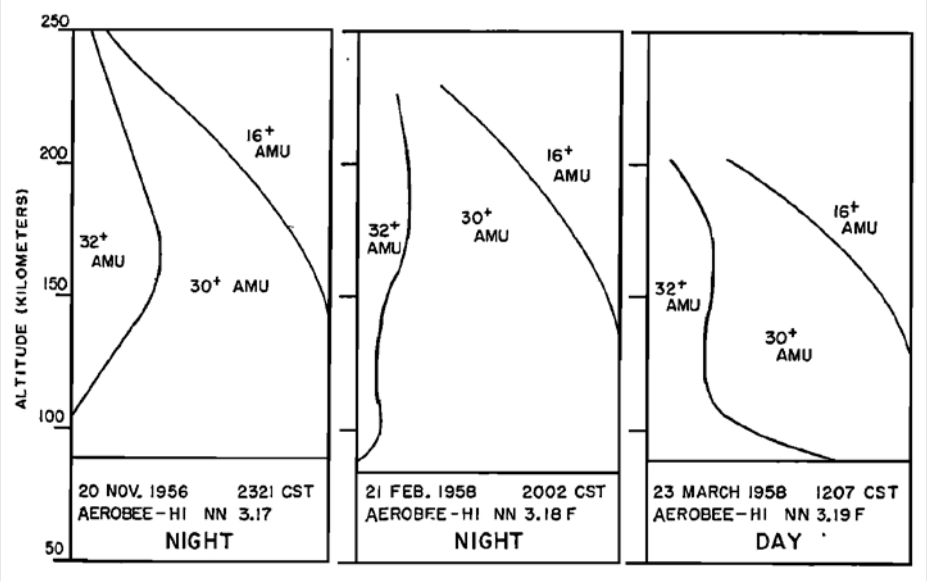


FIGURE 5.31: First measurements of the vertical distribution of the most abundant positive ions over Fort Churchill, Canada, by a mass spectrometer aboard Aerobee rockets in 1956 and 1958. Source: C.Y. Johnson *et al.*, Ion Composition of the Arctic Ionosphere. *J. Geophys. Res., 63*, 443-444, 1958.

[222] Charles Y. Johnson, born in 1920, graduated from the University of Virginia in 1942. After serving in the US Navy during the Second World War, he joined the Cosmic Rays Section of the Naval Research Laboratory. He headed the Air and Ion Composition Section from 1954 to 1958, and the Aeronomy Section until his retirement.

Other ions are also detected at much lower concentrations; these are metal ions, particularly sodium, magnesium, and calcium ions. Above 82 km, the most abundant ions are NO^+ and O_2^+.

Studies based on mathematical models are used to interpret the observations. They confirm that the most abundant ions in the *D* region of the ionosphere are NO^+ and O_2^+. Both are produced by direct ionization under the effect of solar radiation, but the latter is also produced by charge transfer between the primary ion N_2^+, also produced by direct ionization, and the oxygen molecule O_2. This latter process explains the low concentration of N_2^+ in this region of the ionosphere. In the lower part of region *D*, hydrated protons of the type $H^+(H_2O)_n$ (where n is an integer) observed by mass spectrometry are formed from NO^+ in the presence of water molecules. Finally,

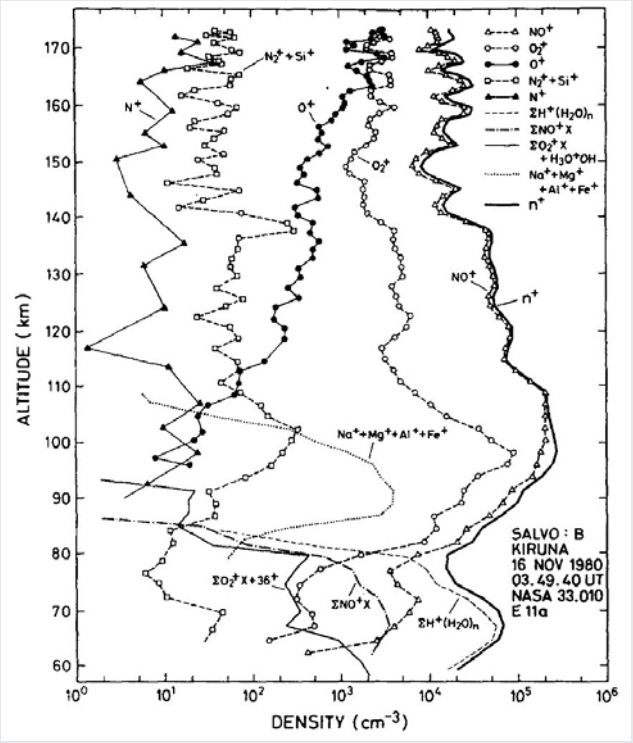


FIGURE 5.32: Vertical distribution of positive ion concentration (in number of ions per cubic centimeter of air) in Kiruna, Sweden, on November 16, 1980 at 3:50 UT, as measured by Ernest Kopp and colleagues at the University of Bern. The measurements were made between 60 and 170 km altitude by a mass spectrometer on board a Taurus-Orion rocket. The dominant ions in the thermosphere above 120 km are NO^+, O_2^+, O^+ and N_2^+. In the mesosphere below 80 km, the dominant ions are H^+ protons, around which water molecules aggregate ($H^+(H_2O)_n$ with n = 1, 2, 3, ...). Other aggregates that form around NO^+ and O_2^+ ions are also present, but in smaller quantities. Between 85 and 95 km, a layer of metal ions (Na^+, Mg^+, Al^+ and Fe^+) is also present, resulting from the vaporization of meteorites as they enter the atmosphere. The positive ions of mass 28 detected by the spectrometer correspond to the N_2^+ ion above 122 km and the Si^+ metal ion below this level. Source: Kopp *et al.*, *J. Atmos. Terr. Physics,* 47, 301-308, 1985.

negative ions are also present in large quantities in the *D* region, formed by the attachment of an electron to an oxygen molecule. Complex mechanisms lead to the formation of negative ions such as CO_3^-, NO_2^- and NO_3^-.

In region *E,* the ions initially formed are O_2^+ and N_2^+, but, as in region *D*, the N_2^+ ion transfers its positive charge to the O_2 molecule to form the O_2^+ ion. The primary ion N_2^+ also reacts with the oxygen atom O to form NO^+ or O^+.

The *F* region is dominated by direct ionization of the oxygen atom and, at very high altitudes, of the hydrogen atom. Direct recombination of O^+ is very slow, so it occurs indirectly through reactions of O^+ with N_2 and O_2 to produce the ions NO^+ and O_2^+, respectively, and through recombination of the latter two ions with an electron.

6
The Protective Ozone Layer

In a stunning article published in the *New York Times* on November 7, 1985, journalist Walter Sullivan (1918-1996) announced to the public what Joseph Farman and his colleagues at the *British Antarctic Survey* had discovered a few months earlier: for the past ten years, during the southern hemisphere spring, a giant hole had formed in the ozone layer over Antarctica. The phenomenon discovered thanks to systematic measurements carried out since 1957 at the Hadley Bay polar base, was also observed from space by NASA satellites. The cause of this large-scale disturbance was not known at the time of the first observations, but several hypotheses were put forward. One referred to a change in weather conditions, while others suggested a variation in solar activity. Some, including Farman, attributed the disruption to a chemical effect resulting from human activity, blaming chlorofluorocarbons, which were produced by industry and used in a wide range of applications. However, the mechanism behind the rapid destruction of ozone in September and October was not yet known. In any case, long-term ozone depletion would expose the Earth's surface to increased doses of solar ultraviolet radiation, with potentially devastating consequences. Indeed, a thinning of the ozone layer would lead to a significant increase in the incidence of human skin cancer and a significant reduction in agricultural yields.

This information, widely disseminated by the international press, caused a psychological shock not only among the public but also among scientists, who had not anticipated a phenomenon whose origin was not understood. The idea of artificially creating a hole in the ozone layer was not new, but for geophysicists, the phenomenon had to be artificial rather than spontaneous and unexpected. In fact, in the early twentieth century, astronomers had proposed creating a temporary hole in the ozone layer over their telescopes so as not to interfere with their observations by absorbing too much incoming solar radiation. During the Cold War, U.S. meteorological officials considered creating a hole in the ozone layer over the Soviet Union to deprive the local population of food resources that would have been altered by the excess ultraviolet radiation. Calculations by Oliver Reynolds Wulf[223] (1897-1987) at the California Institute

[223] A chemist, physicist and meteorologist, Wulf, a member of the American Academy of Sciences, is renowned for his research into nitrogen fixation, ozone and atmospheric dynamics. He first worked for the US Department of Agriculture, then for the Weather

of Technology in Pasadena, at the suggestion of Harry Wexler[224] (1911-1962), Chief of Scientific Services at the U.S. Weather Bureau, showed that an annual injection of 100,000 tons of bromine into the stratosphere would have been sufficient to prevent ozone reformation at latitudes above 65 degrees north.

When the problem of stratospheric ozone[225] received special attention in the 1970s and 1980s, it was because of the potential impact of human activities on a layer that is fragile but essential to sustaining life on Earth. The issue of anthropogenic ozone depletion is discussed further in Chapter 10. In the following pages, we trace the path that led several chemists in the nineteenth century to identify the presence of a new substance in the atmosphere, then, in the early twentieth century, to determine the height of the ozone layer, and finally, beginning in the 1930s, to identify the chemical production and destruction mechanisms of this molecule.

Ozone in the Laboratory

On March 13, 1839, Christian Friedrich Schönbein (1799-1868), a professor at the University of Basel in Switzerland, attended a meeting of the *Schweizerische Naturforschende Gesellschaft*. He reported the results of an experiment he had just performed on the electrolysis of water, during which a strange, persistent odor filled his laboratory. Was it a gas produced by electrolysis? And if so, which gas? Or were they fine particles that came off the electrodes when a current flowed through the device? We had to wait nearly 40 years for the answer to these questions.

Schönbein was self-taught. He was also a picturesque character who loved humor, good food, and never refused a good glass of wine. After completing primary school in his native Metzingen, Germany, in 1812, he was apprenticed to a chemical factory in Böblingen, where he worked for seven years. This time in a private company allowed him to become familiar with chemical processes, and at the age of 21, he did not hesitate to take a chemistry examination in Tübingen - the only examination he ever took. In 1820, Schönbein became manager of a chemical plant in Hemhofen, near Erlangen, and decided to take some courses at the city's university, where he met the famous chemist Justus von Liebig. He completed his education by taking further courses at the University

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Bureau and finally for the University of Chicago Meteorological Institute. He joined the California Institute of Technology in 1945, where he conducted research into solar-terrestrial magnetism, geomagnetism and large-scale atmospheric circulation.

[224] A former colonel attached to the army weather service during the Second World War, Wexler became head of scientific services at the US Weather Bureau (predecessor of NOAA) in 1946. He supported Roger Revelle and Charles Keeling's initiative to systematically measure atmospheric CO_2. He is considered the father of meteorological satellites and proposed the development of an international system of Earth observations. He was interested in climate change and the possible action of bromine and chlorine as ozone-destroying agents.

[225] See for more details: Brasseur, G. P., *The Ozone Layer. From Discovery to Recovery*, American Meteorological Society, 264 pp., 2019.

of Tübingen. In 1826, he moved to Epsom, England, to teach mathematics and science at the private school *The Cedars*. A year later, he moved to Paris to study physics and chemistry at the Sorbonne. During his travels, he met several distinguished scientists, including the specialist of electromagnetism, Michael Faraday (1791-1867), physicist Joseph Louis Gay-Lussac, chemist Jacques Louis Thénard, and physicist André-Marie Ampère (1775-1836), a professor at the Collège de France. Schönbein was only 29 years old when he became an extraordinary professor at the University of Basel, where he taught chemistry and physics in the absence of the professor in charge, Peter Merian (1795-1883). His lectures were so popular that the university awarded him an honorary doctorate in 1829. He was also honored in several European countries and elected a corresponding member of various academies, including the Prussian Academy of Sciences, the Leopoldina Academy in Germany, and the Académie des Sciences de Paris. In 1835, he was appointed full professor of chemistry in Basel.

Schönbein's discovery was strange and, above all, unexpected. The Basel professor was convinced that the phosphorus-like odor produced in his laboratory was the result of the formation of a gas, and his university colleague, the philologist Wilhelm Vischer-Bilfinger (1808-1874), a specialist in ancient Greek, suggested that this odoriferous property be given the German name *"ozon"*, from the Greek (*ozein*, to smell). The odor was like that observed around 1800 by the Dutch physician Martin van Marum (1750-1837) when he created an intense electric discharge using the impressive electrostatic generator he had built in Harlem. It was also similar to the odor perceived by Schönbein himself when lightning struck the church tower near his home.

Schönbein also made a name for himself with the discovery of the fuel cell in 1838. Eight years later, he accidentally discovered the explosive nature of nitrocellulose. While his wife Emilie Benz was out of the house, he tried a quick experiment in the kitchen, but accidentally spilled a bottle containing a mixture of nitric and sulfuric acid. To wipe the kitchen table before his wife returned, he used a cotton apron, which he then dried near the stove. To his surprise, the apron "exploded". The reaction between nitric acid and the cellulose in the piece of cotton produced cellulose nitrate, a powerful explosive.

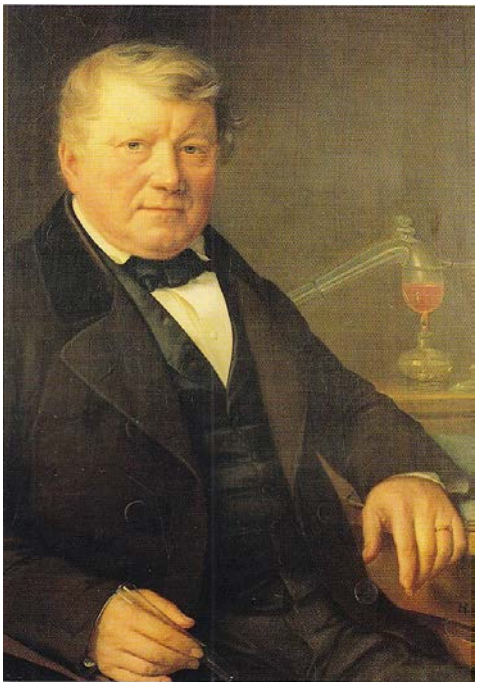


FIGURE 6.1: Christian Schönbein.

It would be several decades before the chemical formula for ozone was established. Schönbein believed that the gas produced by electrolysis or an electric spark was a compound containing oxygen and hydrogen,

perhaps the radicals HO_3 or HO_2 or hydrogen peroxide (H_2O_2), a molecule discovered by his colleague Jacques Thénard. Or maybe, it was a halogen species (chlorine or bromine). However, in an 1845 letter to the mathematician and physicist François Arago (1786-1853), the Geneva physics professor Arthur de la Rive (1801-1873) noted that:

> "Ozone comes only from oxygen, and the simplest and most direct way to demonstrate this is to pass a succession of electric sparks through the oxygen."

This led Jean-Charles Galissard de Marignac (1817-1894), professor of chemistry at the Académie de Genève, to propose that ozone is an allotropic form of oxygen[226]. Schönbein disputed this conclusion. However in 1850, he had to face the facts: experiments clearly showed that ozone contains only oxygen atoms.

Following the findings of his Geneva colleagues, Schönbein suggested that ozone consists of a negatively charged oxygen molecule. To achieve electrical neutrality, a second, positively charged form of oxygen must therefore exist. The latter was not observed, but Schönbein, in a letter to his friend Michael Faraday, gave it the name *antozone* and concluded that ordinary oxygen resulted from the recombination of ozone and antozone. Research was conducted to detect this unknown substance, notably by Georg Meissner (1829-1905) in Göttingen, but although he identified cigarette smoke, chimney emissions, and gunpowder as antozone, his conclusions were not convincing.

The second, more plausible theory followed from de la Rive's and Marignac's discoveries with the work of Jacques-Louis Soret (1827-1890), a former student of Marignac's, who used an ingenious method based on Graham[227] scattering to accurately measure ozone density in 1863. He concluded in 1865:

> "The facts lead us to assume that ozone is an allotropic state of oxygen consisting of a molecular grouping of several atoms of this body. One of the simplest hypotheses in this respect is the one I indicated earlier, in which we consider the ordinary oxygen molecule as formed of two OO atoms, and the ozone molecule as formed of three OOO atoms."

Schönbein would no doubt have learned of Soret's conclusions a few months before his sudden death in Baden-Baden, on his way back to Basel after being treated in Bad Wildbad for gout attacks. In any case, by 1865, everyone agreed that the embarrassing story of the *antozone* was now over: this imaginary substance did not exist.

The ozone problem was of great interest to the scientific community, so much so that the physician Thomas Andrews (1831-1901), Professor of Chemistry at Queen's College Belfast, who had shown that the ozone molecule was heavier

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[226] Allotropic is the property of certain chemical elements, such as oxygen, to exist in several different forms in the same physical state. The element's atoms are linked together in different ways.

[227] A law formulated in 1848 by Scottish chemist Thomas Graham (1805-1869), which states that the rate of diffusion of a gas is inversely proportional to the molecular mass of the particles. When a gas diffuses in relation to a second gas, the law makes it possible to determine the molecular mass of the first if that of the other gas is known.

than that of oxygen, thus supporting Soret's conclusions, began an article published in 1855 with the following words

> "Among the many interesting subjects which the researches of modern chemists have brought to the fore, few are more remarkable than the substance to which the name ozone has been given."

With this enthusiasm for ozone-related issues, laboratory work multiplied in the second half of the nineteenth century. The main chemical and thermodynamic properties of the molecule were established and, in 1881, the British chemist working in Dublin, Sir Walter Noel Hartley (1845-1913), showed that ozone strongly absorbs ultraviolet radiation at wavelengths between 230 and 300 nm. Measurements at other wavelengths were carried out by James Chappuis (1854-1934) in France and by astronomer Sir William Huggins (1824-1910) and his wife Lady Margaret Lindsay Huggins (1848-1915) in England. This work was important because it highlighted a very important role for ozone: that of protecting living things from the harmful effects of ultraviolet solar radiation. Without ozone in the atmosphere, life on Earth as we know it would not be possible.

Ozone in the Air

Most of the early work on ozone was done in the laboratory. But the question soon arose: was this odorous substance, known since 1865 to be an oxygen-bound gas, an element in the chemical composition of the atmosphere? Of course, Schönbein himself had noticed the characteristic smell of ozone in the vicinity of thunderstorms, which seemed logical to him, since this substance was formed by an electric flash passing through the air. However, to answer this question more fully, it was necessary to establish a method for detecting the presence of ozone in the air and measuring its concentration.

Chemists who know that ozone chemically reacts with potassium iodide (KI) to form the iodine molecule (I_2) and potassium hydroxide (KOH)[228] suggested that a sheet of paper impregnated with potassium iodide and starch be exposed to air for 12 to 24 hours and that the blue or indigo color of the starch complex formed, containing the iodine molecule, be observed periodically. The ozone content of the ambient air could be determined by comparing it to a color scale: the lighter the blue, the more ozone was present in the air. The ozone measurements were therefore expressed in relation to a scale that varied from 0 to 10, depending on the intensity of the color observed. This technique, on which Schönbein's "ozonoscope" was based, was not very accurate, however, because it was subject to interference from other gases that may have been present in the air and reacted with potassium iodide. Nevertheless, this measurement technique was widely used.

In 1858, in Rouen, France, Jean-Auguste Houzeau (1829-1911), a professor at the École d'Agriculture du Département de la Seine Inférieure, discovered the

[228] $2KI + O_3 + HO_2 \rightarrow 2\ KOH + I_2 + O_2$

presence of ozone in the atmosphere by measuring a reaction between air and a mixture of iodine and arsenic. He decided to carry out systematic measurements from 1861 to 1870 and concluded that ozone was a permanent compound in the atmosphere. He also observed that this gas was more abundant in the spring and less abundant in November.

At the time, the ozone issue received a great deal of attention and was even subject to some controversy. Many believed that the presence of this gas in the atmosphere had beneficial effects on health, if not, as some claimed, harmful effects. Statistical analyses, no doubt superficial, suggested that human mortality increased as ozone levels decreased. In the city of Lyon, where instruments did not detect the presence of ozone in the air, the cholera rate was particularly high. In other words, ozone would be responsible for the destruction of microbes. In his book *Ozone and Antozone*, published in 1873, Cornelius B. Fox, M.D., a member of the Royal College of Physicians and Surgeons of England, wrote that ozone

> "should be pumped into our mines and cities, and dispersed through [...] sick rooms, and in crowded localities of the poor, or wherever the active power of the air is reduced and poisons are generated. [...] Ozone can be easily disseminated through public buildings, theaters and other confined atmospheres, where large numbers of people are accustomed to congregate, in order to maintain the purity of the air."

Ozone, which is a powerful oxidizing agent, plays another role: it disinfects water and purifies the air. This is why, even before Soret's chemical characterization of the gas, ozone generators were produced as early as 1857 and marketed, notably in Berlin by Ernst Werner von Siemens (1816-1892).

Thanks to the techniques that became available, ozone measuring stations were set up everywhere. But it was in Paris, in the Parc Montsouris, that sustained ozone measurements were made between 1876 and 1910, thanks to the efforts of Albert Lévy (1844-1907).

Ozone Measurements in Parc Montsouris, Paris

Albert Lévy was a talented scientist and a skilled experimenter. A prolific popularizer, he published a work on the *History of Air* in 1879, as well as interesting biographies of Galileo, Lavoisier, and Arago. His contemporaries regarded him as modest and sympathetic, an independent character, a brilliant and witty orator, and a universally appreciated man of great kindness.

After graduating from the École Polytechnique in 1866, Lévy was hired by director Urbain Le Verrier (1811-1877) at the Imperial Observatory in Paris. Le Verrier was one of the most renowned specialists in celestial mechanics. A supporter of political absolutism, he swore allegiance to Napoleon III after the coup d'état of December 1851 and the proclamation of the Empire. He held several political offices, including that of senator. He enjoyed a great reputation among his fellow astronomers for his mathematical explanation of the irregularities in the motion of Uranus, which suggested the existence of a previously unknown

planet whose position he predicted. The planet was first observed by the Berlin astronomer Johann Gottfried Galle (1812-1910), who had received the probable coordinates of its position from the French astronomer. This is how the planet Neptune was discovered. But Le Verrier was also an authoritarian, tyrannical and vindictive director who didn't tolerate the slightest criticism and fired people who didn't share his views. The Imperial Observatory thus became a battleground where tensions ran high. In January 1870, the situation was so intolerable that thirteen astronomers, including Albert Lévy, collectively resigned. Despite the Emperor's benevolence, the Minister of Public Instruction, Émile Alexis Ségris, relieved Le Verrier of his duties and obtained his dismissal from Napoleon III. The new director, Charles-Eugène Delaunay (1816-1872), who was also Le Verrier's sworn enemy, didn't seem to appreciate the talents of Albert Lévy, who was given the unattractive job of secretary-accountant in charge of the library. In a note written on July 8, 1871, to Armand Du Mesnil, the director of higher education in Paris, Delaunay complained about Lévy's performance:

> "The duties of the equipment secretary are completely useless. Poor Lévy, who doesn't realize this, makes their uselessness even more obvious by his inertia, or to use the right word, his laziness. He does nothing. Do you know how he keeps the archives and the library? It's by not touching the books or the manuscripts."

In August 1872, Delaunay drowned in a boating accident in the port of Cherbourg, and just as the Empire gave way to the Third Republic, Le Verrier was reinstated as director of the Observatory on February 13, 1873, by the new President of the Republic, Adolphe Thiers (1797-1877), who was a political friend. A few months later, Lévy left the Paris Observatory and joined the Montsouris Observatory in 1873, where he was appointed physicist. Two years earlier, the observatory had moved to the Palais du Bardo, a building designed to represent Tunisia at the 1867 World Fair in Paris. Dismantled and then reassembled in the Parc Montsouris, the palace survived the siege of Paris in 1870 and was damaged by fighting in the park following the Parisian uprising during the Commune of 1871. Founded in 1869 by the geologist and meteorologist Charles Sainte-Claire Deville (1814-1876), the Observatoire du Parc Montsouris developed in a

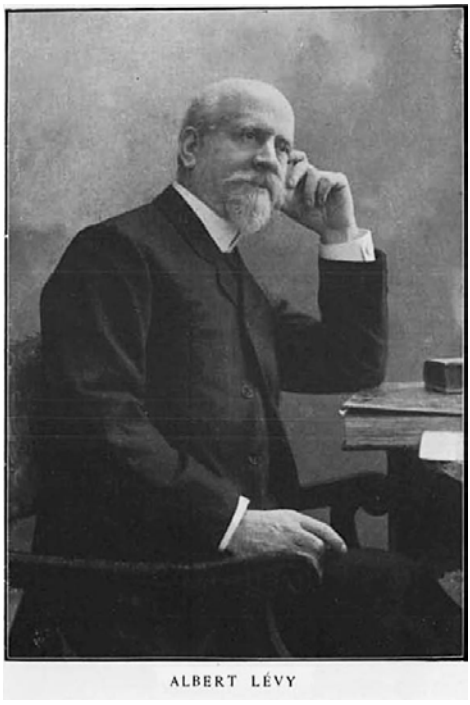

ALBERT LÉVY

FIGURE 6.2: Albert Lévy. Source: Albert Lévy 1844-1907, Notice nécrologique, Annuaire de l'Association Amicale des Anciens Élèves du Lycée Charlemagne, Paris, 1908.

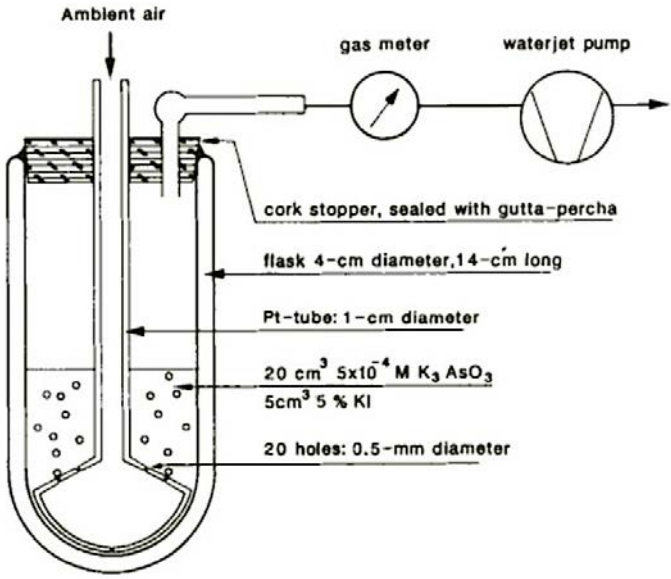


FIGURE 6.3: Ozone measuring instrument in Parc Montsouris, Paris. Ambient air is drawn into the tube and passes through a solution of K_3AsO_3 and KI. The device was placed on a balcony of the observatory, 5 meters above the ground.

difficult context marked by the Franco-Prussian War of 1870-1871 and the Paris Commune. Initially attached to the Paris Observatory, the institution became independent in 1878, despite Le Verrier's opposition. The brilliant chemist Edme Hippolyte Marié-Davy (1820-1893) headed the institution until 1886.

At Montsouris, Albert Lévy, in charge of chemical and bacteriological air analysis, developed an instrument for measuring ozone by passing a known quantity of ambient air through a 3% solution of potassium iodide (KI) in a chamber containing a potassium arsenite compound (K_3AsO_3). The ozone concentration in the air was derived from the rate of conversion of arsenite (AsO_2^{3-}) to arsenate (AsO_4^{3-}), with potassium iodide acting as a catalyst. Measurements indicated that the relative concentration of ozone varied between 5 and 15 parts per billion[229], which is much lower than the levels measured in Europe today (generally around 40 to 50 parts per billion). The increase in ozone concentrations since the beginning of the twentieth century was largely due to rising emissions of pollutants such as nitrogen oxides and volatile organic compounds from automobiles. A recent re-evaluation of ozone concentration measurements suggests that the method used by Lévy was sensitive to oxidants other than ozone that were probably present in the atmosphere around Paris. At the beginning of the nineteenth century, the air was polluted by emissions of sulfur dioxide, produced by burning coal for heating, and ammonia, produced by the 80,000 horses and 5,700 cows present in the French capital. Lévy himself recognized that his measurements were likely to be distorted by the effect of "reducing gases" in

[229] One part per billion here means that one ozone molecule per billion air molecules is measured in the air.



FIGURE 6.4: The Palais du Bardo, which has housed the Meteorological Observatory in Parc Montsouris since 1876, represented Tunisia at the Universal Exhibition of 1867. The city of Paris bought it and rebuilt it in the park in 1869. The state installed the meteorological observatory and, in 1893, a chemical and bacteriological air analysis department. In 1974, the palace was abandoned and left to rot, and in 1991 it was completely destroyed by fire.

the atmosphere, so he introduced a correction to account for this effect. He also noticed that the amount of ozone measured varied with the direction of the wind; it was higher when the wind came from the center of the city and lower when the wind came from the countryside.

In addition to his measurements with the rather complicated chemical method he had adopted, Lévy made parallel measurements with the ozonoscope developed by Schönbein, with which systematic observations were made throughout Europe and even on other continents. This allowed him to establish a relationship between the values corresponding to Schönbein's blue/indigo

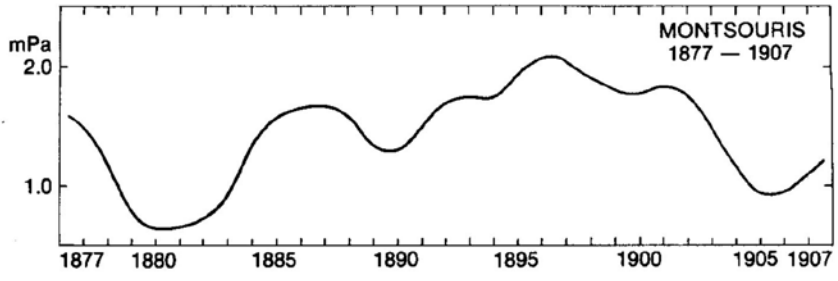


FIGURE 6.5: Trends in ozone partial pressure measured at the Parc Montsouris Observatory between 1877 and 1907. Measurements have been smoothed to filter out daily fluctuations. 1 hPa corresponds to approximately 10 parts per billion. Source: Bojkov R., *J. Climate and Appl. Meteorology*, March 1986, American Meteorological Society.

color scale and the absolute value of the ozone concentration in the air. The equivalence between the two techniques was not easy to establish, as both were affected by chemical interferences and variable humidity levels. However, with the uncertainties inherent in this conversion, it became possible to convert the indices (from 0 to 10) associated with the ozonoscope measurements into actual concentrations. This led to the conclusion that the average ozone concentration in Europe at that time was 14 ± 2.5 parts per billion. These values are important because they are often used as a reference to characterize a pre-industrial situation. This conclusion is now being questioned because the impact of human activity was already considerable at that time and the quality of the measurements is questionable.

An Ozone Layer in the Stratosphere

A few years after Albert Lévy's death, major advances were made at the University of Marseille. Maurice Paul Auguste Charles Fabry (1867-1945), known as Charles Fabry, wanted to explain why ultraviolet solar radiation with wavelengths below 300 nm was almost completely absorbed in the atmosphere, as had been observed in 1879 by Marie Alfred Cornu (1841-1902), professor at the École Polytechnique in Paris. Together with his colleague Henri Buisson (1873-1944), Fabry measured the absorption coefficient of ozone as a function of wavelength in the laboratory and then photometrically determined the intensity of the solar radiation reaching the Earth's surface. The two researchers deduced that the strong absorption of solar radiation was due to ozone, and in an article published in 1913, they concluded:

> "To produce this absorption, the atmosphere must contain a quantity of ozone equivalent to a 5-millimeter layer of pure ozone at normal pressure."

Fabry and Buisson had just determined for the first time the amount of ozone integrated between the ground and the outer atmosphere. This quantity is known as the ozone *column*. They added that if the quantity they measured were uniformly distributed with altitude, the concentration on the ground should be 600 parts per billion, 40 to 60 times higher than the values measured on the ground by Lévy in Paris. The two scientists concluded:

> "The most likely hypothesis is that ozone exists only in the very top of the atmosphere, where it is produced by the extreme portion of the sun's ultraviolet radiation, which, being strongly absorbed by oxygen, can act only on the highest layers of the atmosphere."

Research in Marseille was interrupted during World War I but resumed after the armistice. Fabry and Buisson refined their measurements and concluded that the thickness of the ozone column was 3 millimeters rather than 5 millimeters. Measurements taken between May 21 and June 23, 1920, showed that the column varied irregularly between 2.85 and 3.35 millimeters. Two questions remained unanswered: first, does the average ozone column vary with geographic location and season, and second, at what altitude is ozone confined?

Global Distribution of Stratospheric Ozone

The first question was answered by Gordon Miller Bourne Dobson (1889-1976). This British scientist, working at the University of Oxford, thought that the temperature rise above 12 km observed by Léon Teisseranc de Bort (1855-1913) and Richard Assmann (1845-1918) was due to the absorption of solar radiation by ozone, which was probably very abundant in the stratosphere. Dobson therefore built a spectrograph based on the one designed by Fabry and Buisson. By measuring the intensity of solar radiation at two nearby wavelengths, Dobson deduced the value of the ozone column. This is now expressed in *"Dobson units"*, which correspond to one hundred times the thickness of the layer in millimeters under standard conditions of pressure and temperature. The advantage of the Dobson spectrograph is that it is small enough to be sent and used anywhere in the world. The first observations made in Oxford over 200 consecutive days showed the variability of the ozone column with meteorological conditions: the ozone column was generally highest when atmospheric pressure was lowest. The opposite occurred during anticyclonic conditions. The most important finding was that the average ozone column value varies with the season, being highest in the spring (March and April) and lowest in the fall (October and November).

To determine the global distribution of ozone, Dobson decided to build several spectrographs, calibrate them against a reference instrument, and send them to different countries, first in Europe and then in more distant regions. After each measurement, the photographic plates were sent back to Oxford, where the data were processed and analyzed. As this was a titanic task, Dobson decided to replace the photographic plates with a photoelectric cell that provided direct readings of the intensity of solar radiation. These more modern spectrophotometers are still in use today.

Instruments at many latitudes in both hemispheres showed that ozone levels increase with latitude, especially in winter and early spring. Levels observed in the tropics were on the order of 200 Dobson units and varied little over the year. In the Arctic, however, the average ozone column was much higher, reaching about 450 Dobson units in April, but only 250 Dobson units in October. In the Southern Hemisphere, maximum values were measured in October, but unlike the situation in the Northern Hemisphere, they did not occur near the pole, but at about 60 degrees latitude. Dobson noted that at the time of the austral spring (October), there was an ozone minimum at the South Pole, located within the vast vortex of air that surrounds the Antarctic continent, isolating this region from external dynamic and chemical influences. At that time, however, ozone column values over the Antarctic continent were much higher than those observed today. Today, there is a real "hole" in the ozone layer over the Antarctic ice during the austral spring. This will be discussed in more detail in Chapter 10.

The measurements made by this first network of instruments were confirmed by subsequent observations, especially those made from space. The global distribution of ozone, as observed since the 1920s, provides an important constraint for those trying to answer the following questions: How is ozone produced and

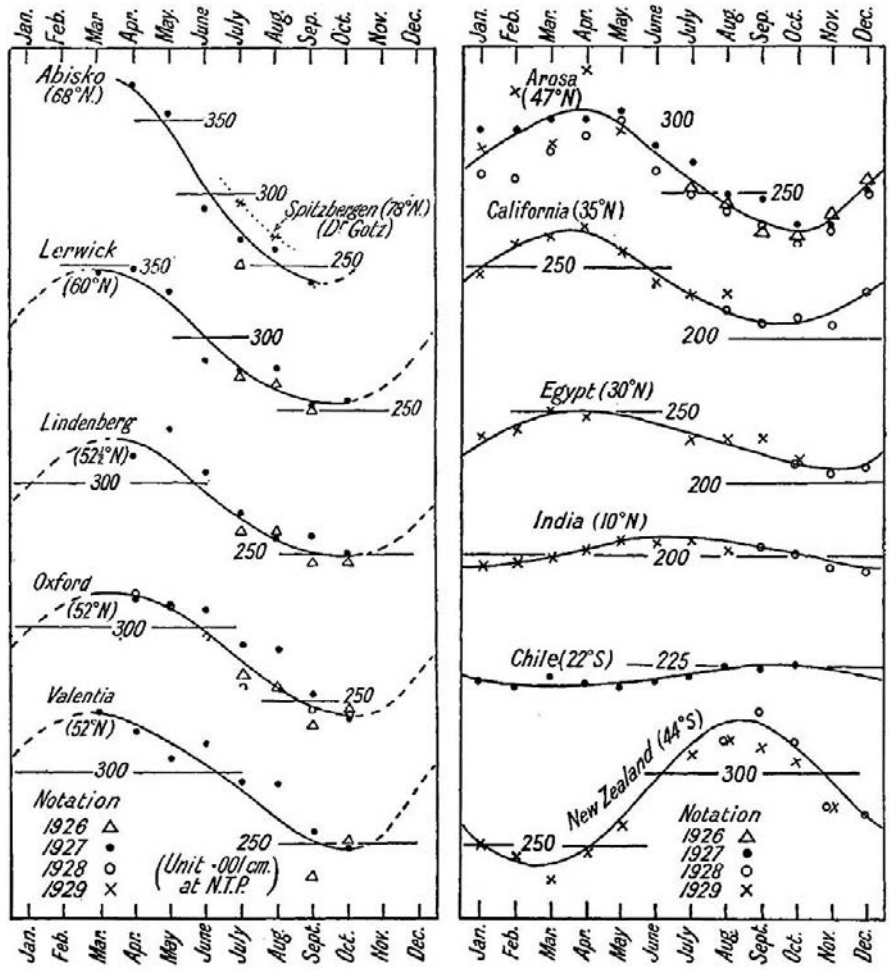


FIGURE 6.6: Seasonal variation of the ozone column [expressed in Dobson units] measured between 1926 and 1929 by several spectrographs installed in different regions of the world, from 68^0N to 44^0S. These first observations showed that ozone abundance peaks in the spring, with the highest values in the northern polar regions. They also highlighted the low amplitude of seasonal variations in the tropics and a 6-month lag in seasonal variations in the Southern Hemisphere. Reproduced from Dobson *et al. Proc. Roy. Soc, London,* A129, 411, 1930.

destroyed in the atmosphere? Why is ozone more abundant at high latitudes than in the tropics? Why is ozone most abundant at the end of the long polar winter night? What are the seasonal values of the ozone column in the polar regions? All these questions remained unanswered for many years.

Charles Fabry and Gordon Dobson were two eminent personalities who made decisive advances in knowledge. In fact, it was Fabry who first pointed out the existence of an ozone layer in the stratosphere, and it was Dobson who showed how the ozone column is distributed on a global scale and according to the seasons.

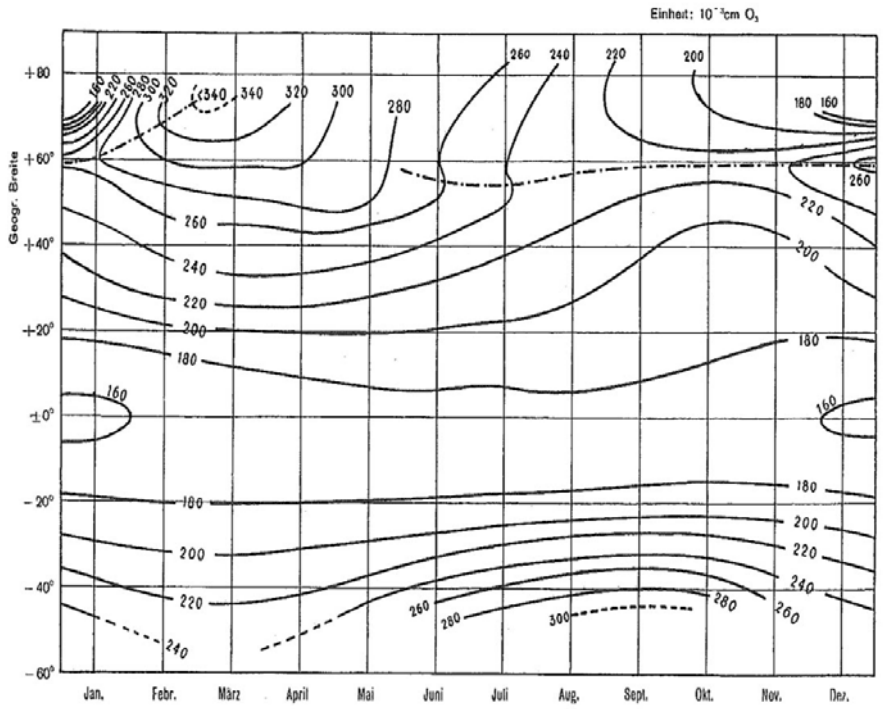


FIGURE 6.7: Variation with latitude and season of the mean ozone column as known from Dobson spectrophotometer measurements in the early 1940s. Values are expressed in Dobson units or 10^{-3}cm of ozone. In the Northern Hemisphere, values peak at latitudes above 75^0N in late February. In the Southern Hemisphere, values are highest around 50^0S between August and October. At that time, little information was available from the polar regions, especially Antarctica. Source: Götz, F.W.P., Der Stand des Ozon problems. *Vierteljahrsschrift der Naturf. Gesellschaft in Zürich*, 89, 250-264, 1944.

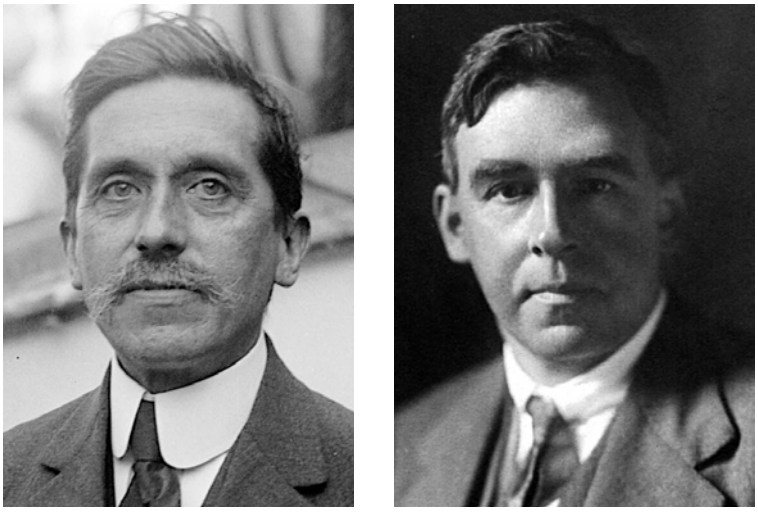


FIGURE 6.8: Charles Fabry (left) and Gordon Dobson (right).

After graduating from the École Polytechnique in Paris and teaching physics at several lycées in France, Charles Fabry joined the University of Marseille in 1894. It was there that he and Jean-Baptiste Gaspard Gustave Perot (1863-1925) developed the famous Fabry-Perot interferometer, which is still in use today. In 1921, Fabry was appointed professor of physics at the Sorbonne in Paris, and in 1927, he took over the chair of physics at the École Polytechnique left vacant by the untimely death of Alfred Perot. During World War II, Fabry retired to Marseille and returned to Paris in 1945. His excellent book on atmospheric ozone, written during the Nazi occupation, was published a few years after his death in 1945.

As for Gordon Dobson, he was hired in 1920 by the Clarendon Laboratory at Oxford University with the assistance of the German Frederick Alexander Lindemann, later Lord and Viscount Cherwell (1886-1957), and scientific advisor to Winston Churchill. After collecting and analyzing thousands of data sets produced by his spectrophotometer, Dobson was still trying to elucidate and understand the mechanisms that explain the accumulation of ozone in the polar regions during winter. New information about water vapor in the stratosphere gained during World War II allowed him to answer this question.

At the beginning of the war, British staff and Royal Air Force pilots were concerned about the number of their aircraft being shot down by German air defenses. For example, in a single raid on the city of Nuremberg, no fewer than 93 aircraft were lost. These planes were probably detected by the white contrails they produced as they passed overhead. A Canadian-born meteorologist, Alan West Brewer (1915-2007), hired by the British Met Office in 1937, was transferred to Bascombe Down, a military aircraft test site on the southeastern outskirts of the town of Amesbury, Wiltshire, England, to study the processes responsible for the formation of these aircraft contrails. Brewer worked directly under Dobson's supervision and interacted with another renowned British scientist who had recently graduated from Cambridge University: the physicist Richard Mead Goody (1921-2023).

To solve the problem of aircraft tracks, and especially to understand the lack of contrails in the stratosphere, Brewer developed a new type of hygrometer. He took temperature and humidity measurements from high-altitude aircraft, including a flying fortress, the *Boeing B17*. This plane was part of the fleet of six large aircraft that Roosevelt gave to Churchill to help the war effort. Further measurements were taken from the *Mosquito* aircraft as it reached higher altitudes and entered the stratosphere. These observations show that the stratosphere is much drier than the lower layers of the atmosphere. Therefore, contrails from high-altitude aircraft do not occur in the higher layers, which are far from saturated. Brewer himself was surprised by his findings and wrote in 2000:

> "I would not have believed before I had started that the air could be so dry, but I saw it with my own eyes. I had plenty of trouble with people convincing them that we could really measure that dryness. [...] Personally, I very soon formed the opinion that the very dry air had come from the equatorial tropopause."

Brewer concluded that there must be an air circulation in the upper atmosphere that transports dry air masses (and thus the chemical species contained in these air masses) from the tropics to the polar regions. In 1949, in a famous article, Brewer wrote

> "The observed distributions [of water vapor] can be explained by the existence of a circulation in which air enters the stratosphere at the equator, where it is dried by condensation, travels in the stratosphere to temperate and polar regions, and sinks into the troposphere."

As early as 1929, Dobson had proposed the existence of such a meridional circulation to explain the high ozone levels observed at high latitudes:

> "The only way in which we can reconcile the observed high ozone concentration in the Arctic in spring and the low concentration in the tropics [...] would be to suppose a general low poleward drift in the highest atmosphere with a slow descent of air near the poles."

But then he changed his mind because this circulation seemed to violate the fundamental law of conservation of momentum. He eventually adopted the idea because it explained not only the transport of water vapor, but also that of ozone between the tropics and mid-latitudes, where it is produced, and the polar regions, where it accumulates during the winter before being destroyed by the action of solar radiation in the spring. The term "Brewer-Dobson circulation" is now commonly used to describe a global-scale phenomenon that explains the transport of chemical species from the equator to the poles above the tropopause. The problem of momentum violation was solved thanks to the work of atmospheric dynamists such as Robert James Murgatroyd (1916-2011), and Michael McIntyre (b. 1941) in England, and James Reed Holton (1938-2004) in the United States. They showed that, in addition to the mean circulation transport highlighted by Brewer and Dobson, there is a mean meridional transport associated with the dissipation of giant planetary waves and the resulting sources of momentum. These waves are generated by the interaction of surface winds and topography, primarily mountain ranges. Meridional circulation explains the transport to high latitudes of volcanic particles ejected during major eruptions or radioactive debris produced by nuclear explosions in the atmosphere.

Brewer, who worked at Oxford University but was born in Montreal, where his parents lived for a short time, returned to Canada in 1962 to establish a meteorology department at the University of Toronto. When he retired in 1976, he returned to the UK to pursue a dream of farming in Devon. He died in Bristol in 2007.

As for Dobson, a music lover, he retired in 1956, which allowed him to play the violin and piano frequently. Nevertheless, he continued his daily ozone observations with the spectrophotometer he had installed at his Shotover Hill estate. His last measurement was taken the day before he suffered a stroke. He died six weeks later at the age of 86.

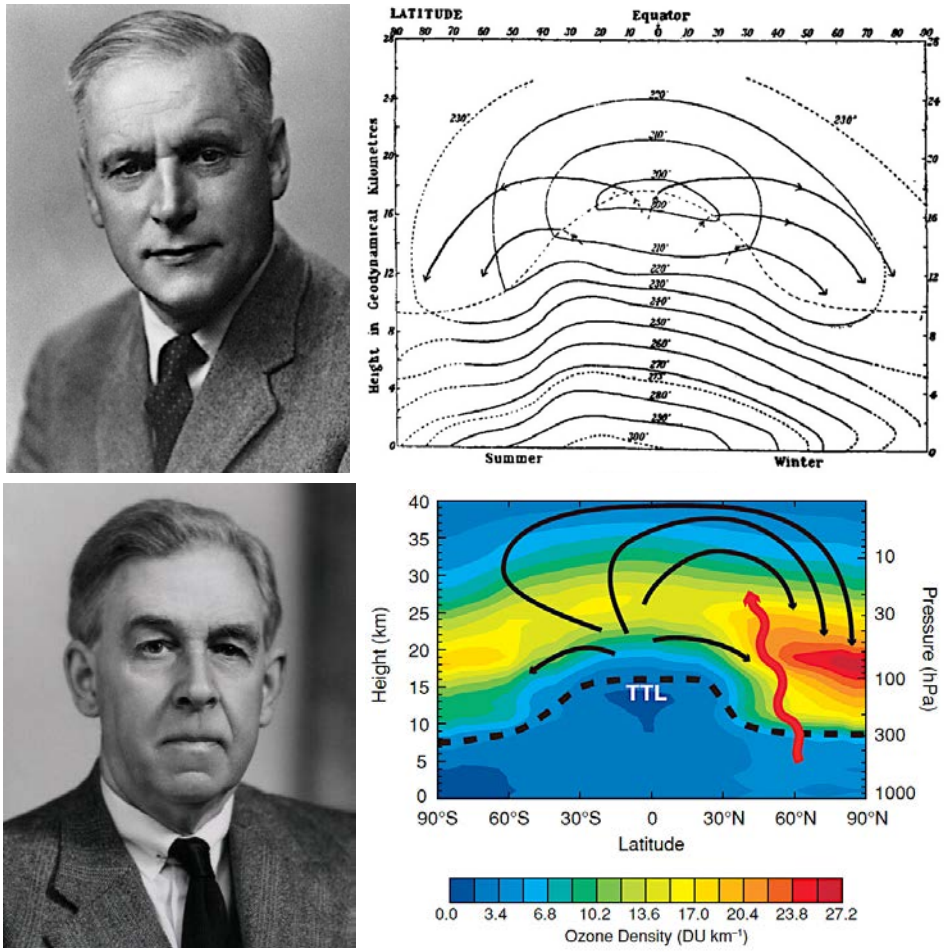


FIGURE 6.9: Top: Alan Brewer and his 1949 depiction of the slow mean meridional circulation between the equatorial tropopause and the polar regions. Bottom: Gordon Dobson and the mean meridional transport of ozone that accumulates in the Arctic polar regions during winter. Planetary wave propagation in the winter hemisphere is symbolized by the red arrow. Source: IPCC/TEAP special report, 2005.

Vertical Distribution of Ozone in the Stratosphere

The early work of Fabry and Dobson did not answer a crucial question: at what altitude is the ozone layer that Fabry located in the stratosphere? It was a German-born physicist working in the Swiss Alpine village of Arosa, Friedrich Wilhelm Paul Götz (known as Paul Götz, 1891-1954), who set out to answer this question. The young Götz first visited Switzerland in 1914 to be treated for tuberculosis at a sanatorium in Davos. Cured, he taught physics at the town's German school for a year, then returned to Germany in 1919 to defend his doctoral dissertation at the University of Heidelberg. He then returned to Davos, where he joined the meteorological observatory founded there by Carl Wilhelm Dorno (1865-1942), a wealthy industrialist who had come from the German town

of Königsberg (now Kaliningrad in Russia) to accompany his daughter, who was also in a sanatorium. Götz didn't get along well with Dorno and decided to move to Arosa to open another solar observing station. Sometime later, Dobson visited Götz and offered to install a copy of the spectrophotometer he had developed in Oxford in the new "Lichtklimatisches Obervatorium" in Arosa. From 1926 to the present, ozone observations have been made almost continuously at Arosa. This is the longest-time series of ozone measurements available today.

In the late 1920s, Götz developed an ingenious method for determining the vertical distribution of ozone concentration. He used the Dobson spectrophotometer, but instead of pointing it toward the sun as normally done, he pointed the optical detector upward, measuring the solar radiation scattered by the sky. The measurement was made over several hours, first in the morning as the sun rose above the horizon, and then in the afternoon as the sun set. Götz found that the ratio of the solar intensities measured at two different but close wavelengths in the ultraviolet decreased continuously with the Sun's elevation but began to increase the moment the Sun's elevation became less than 3.5 degrees. Götz called this reversal *the Umkehr effect*. It is used to derive the vertical distribution of ozone concentration. Dobson was informed by Götz about the method; he applied it in Oxford in January 1931 and obtained a curve that clearly showed the Umkehr effect.

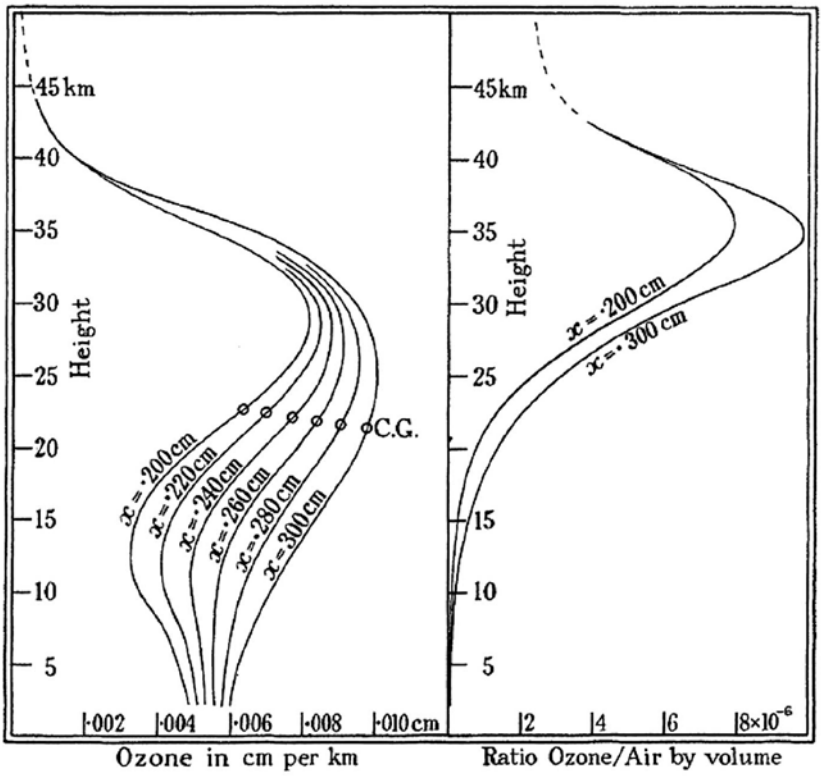


FIGURE 6.10: Vertical distribution of ozone concentration as a function of altitude (0 to 45 km) derived by Götz using the *Umkehr* method. The ozone concentration in the left panel is expressed as the equivalent ozone column in a 1 km atmospheric layer for different total ozone columns. The values in the right panel represent the ozone volume mixing ratio.

The first applications of the *Umkehr* method were carried out in Arosa in 1927 and 1928, but in 1929, in order to position himself at latitudes where the sun is often close to the horizon, Götz decided to continue his measurements on the island of Spitsbergen. He concluded that the ozone layer was at an altitude of about 25 km. In a paper published in 1968[230], Dobson described the method:

> "While in Spitzbergen, Götz took spectra of the zenith skylight while the sun was rising or setting and found that, when the sun was fairly high, the shorter wavelengths decreased in intensity more rapidly than longer wavelengths with increasing zenith distance of the sun. This was to be expected, owing to the greater absorption of the shorter wavelengths. He found, however, that when the sun was very low, the reverse occurred, and the shorter wavelengths decreased in intensity more slowly than the longer ones. He rightly interpreted this as being due to the fact that, when the sun is high, most of the short wavelength zenith skylight is scattered from the direct solar beam below the ozone region, but when the sun is very low the absorption of direct sunlight by the ozone is so great that the amount of light scattered above the ozone region and which passes down to the instrument by the short vertical path becomes pre-dominant. Near the end of 1930 he wrote to me telling me of the effect and suggested that it might be used as a means of estimating the vertical distribution of the ozone in the atmosphere. [...] Then followed a lot of work, both making measurements on the zenith skylight and also trying to work out a theory by which we might calculate the vertical distribution of the ozone."

The Umkehr method was adopted for routine observations in many countries. Götz continued his research in Arosa despite the financial difficulties of the "Lichtklimatisches Obervatorium". Funding from the municipality of Arosa, the canton of Graubünden, the local tourist association, and the railway company, which believed that local tourists would benefit from solar radiation measurements, enabled the observatory to continue operating under Götz's leadership until 1953, and under that of Hans-Ulrich Dütsch (1917-2003), professor at the Swiss Federal Institute of Technology in Zurich, until 1985. Today, the observatory is managed by *MeteoSwiss*, the Swiss meteorological service.

Balloons to Explore the Stratosphere

In the early 1930s, the stratosphere was considered a mysterious region because no human had ever been able to penetrate it. A new frontier of knowledge had to be crossed. Hydrogen or helium-filled balloons would allow a few well-prepared aeronauts to soar to unprecedented heights.

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[230] Dobson, G.M.B., Forty years' research on atmospheric ozone at Oxford: A History. *Applied Optics*, *7*(3), 387-405, 1968.

On May 27, 1931, two Swiss physicists, Auguste Piccard (1884-1962) and his assistant Paul Kipfer (1905-1980) from the Université Libre de Bruxelles (ULB), took to the air above the German city of Augsburg. Their gondola, suspended from a giant hydrogen-filled balloon, was pressurized. The goal of the two scientists was to measure the intensity of cosmic radiation in the various layers they passed through, but their ultimate objective was to be the first to penetrate the stratosphere. The two aeronauts reached an altitude of 51,790 feet (15.8 km), an absolute record at the time, and descended a few hours later before landing on a glacier in the Tyrolean Alps. Two years later, a new record was set, this time by two American aviators, Lieutenant Thomas Greenhow Williams "Tex" Settle[231] (1895-1980) of the US Navy and his instrument operator, Major Chester L. Fordney of the Army. Taking off from Akron, Ohio, in the Century of Progress gondola, the two servicemen reached an altitude of 61,000 feet (18 km) on November 20, 1933. They made the first radio transmissions from the stratosphere, which were broadcast live by several radio stations in the United States. On a subsequent flight in October 1934, Jeannette Piccard (1895-1981), wife of Auguste's twin brother Jean Piccard (1884-1963), became the first woman to reach the stratosphere. On that day, the balloon reached an altitude of 57,979 feet (17.5 km).

The question immediately arised: shouldn't ozone be regularly measured from balloons, manned or unmanned? The Umkehr method developed by Götz to determine the vertical distribution of ozone suffered from a major flaw: the low spatial resolution of the measurement. This led the German physicist Erich Rudolph Alexander Regener (1881-1955), a professor at the Technical University of Stuttgart where he worked with his son Victor H. Regener (1913-2006), to attempt a more direct measurement of ozone in the various layers of the stratosphere. As part of his work to measure cosmic rays, Regener became familiar with the technique of using large rubber balloons inflated with hydrogen. He was convinced that such balloon ascents would make it possible to measure ozone as a function of altitude.

The maximum altitude reached by the instruments was directly related to the use of the rubber that made up the membrane of the balloon. This rubber was not free of small defects that often caused the membrane to tear (sometimes below 20 km). Regener imagined several configurations for his experiments. He succeeded in lifting a 6.5 kg instrument to an altitude of 28 km by tethering four balloons together with a thin rope.

On July 31, 1934, the Stuttgart group launched an unmanned balloon carrying a spectrograph with a detector facing the sun. At various altitudes during the ascent and then during the parachute-dampened descent of the instrument, the intensity of the solar ultraviolet radiation was recorded on a photographic plate, which was collected at the point of impact of the instrument on the ground. Analysis of the solar spectra provided information on the vertical structure of the stratospheric ozone layer up to an altitude of about 30 km.

[231] Settle later became Vice-Admiral.



FIGURE 6.11: Left: Paul Götz. Right: Erich Regener.

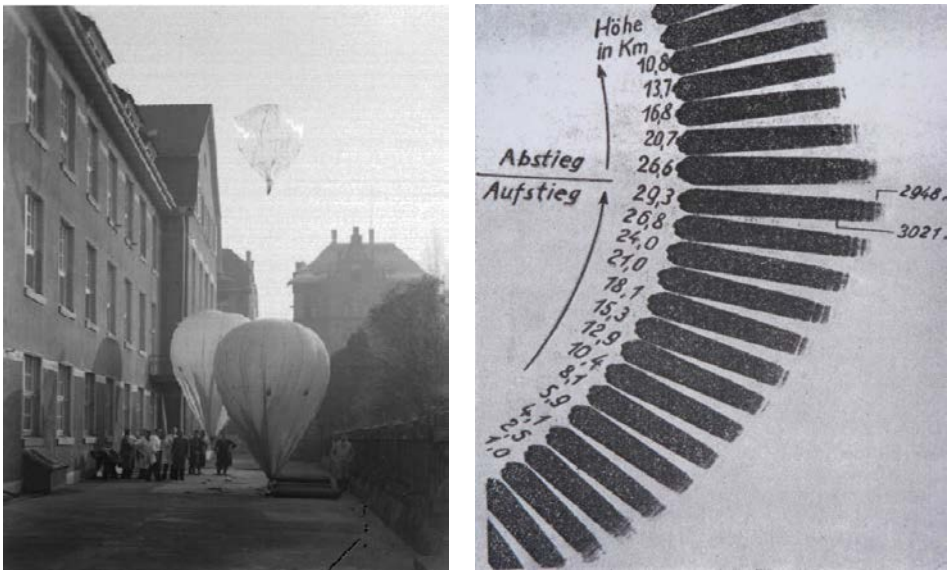


FIGURE 6.12: Left: the launch of a balloon in Stuttgart in 1934 and solar spectrum measurements at different altitudes during the ascent (*Aufstieg*) and descent (*Abstieg*) of the spectrometer. By measuring the absorption as a function of wavelength, the ozone column above the instrument can be determined and the vertical profile of the ozone concentration can be deduced. Source: Regener, E. and Regener V., *Phys. Zeitschr.,* 35, 788-793, 1934.

Regener's work was interrupted by the Nazi regime. The professor was dismissed from his position at the university because his wife had ancestors of Jewish origin. Regener was forced to work independently but eventually joined the *Kaiser Wilhelm Society*[232] where he continued his ozone research. There

[232] The Kaiser Wilhelm Society, the forerunner of the Max Planck Society, aims to promote basic research in Germany. It was founded in 1911 by Kaiser Wilhelm II, after whom it was named. It was funded by private donations and grants from the Prussian government for infrastructure.

he developed an instrument, colloquially known as the *Regener-Tonne*, which he intended to install on a German Aggregat-4 rocket (better known as the V-2 rocket) to measure, he hoped, ozone concentrations up to an altitude of 70 km. Despite the encouragement of *Wernher von Braun* (1912-1977), director of the Peenemünde space center on the Baltic Sea, no rockets were made available to Regener except one for a technical test; the V-2s were all requisitioned for the war effort. At the end of hostilities, the Regener Tonne suddenly disappeared, but the instrument was found a few months later in the desert of New Mexico, where American scientists were using rockets confiscated in Germany to make measurements in the upper atmosphere. After the war, Regener was reinstated at the University of Stuttgart and in 1948 became one of the directors of the Max Planck Society.

In the United States, World War I veteran Captain Albert William Stevens (1886-1949) convinced his superiors in the U.S. Army to organize a manned flight to measure the intensity not only of cosmic rays but also of solar ultraviolet radiation. From these measurements, it would be possible to derive the vertical profile of ozone concentration.

The mission, named *Explorer*, was sponsored by the National Geographic Society and the U.S. Army. The balloon and gondola, carrying Major William Ellsworth Kepner (1893-1982), Lieutenant Orvil Orson (Arson) Anderson (1895-1965), and Captain Stevens, took to the skies over the Black Hills of South Dakota on July 28, 1934. Unfortunately, at an altitude of 63,000 feet, the aeronauts discovered that the balloon envelope had ruptured, and hydrogen was escaping into the atmosphere. The balloon began to descend, and the situation became dangerous. After descending to an altitude of 2,000 meters, the three men decided to abandon the gondola and use their emergency parachutes to return to *terra firma*. At this point, the hydrogen that had been partially trapped inside the ruptured balloon envelope suddenly burst into flames, and the gondola crashed to the ground. Before parachuting out and landing safely in the American countryside, the crew managed to detach the solar radiation spectrometer and let it slowly descend to the ground under the protection of a parachute. The data was recovered, and ozone measurements were taken.

A second attempt, called *Explorer II*, took place on November 11, 1935. This time, the neoprene latex balloon was inflated with helium, and only two men, Albert Stevens and Orvil Anderson, took their places in the gondola. Launched again from the Black Hills, the balloon reached an altitude of 72,395 feet (22 km), setting a new record. For the first time, a live radio link was established from the stratosphere, and the aeronauts shared their impressions with the world over the airwaves of the National Broadcasting Company in Rapid City. They also talked with the crew of the Pan American Airways "China Clipper". Measurements of solar ultraviolet absorption during the flight provided a new vertical profile of ozone concentration; the results were compared with those obtained during Regener's unmanned flight in Germany.

After this initial exploratory work, which required a heavy infrastructure, small automatic probes carried by small balloons were used to measure the vertical distribution of ozone with high precision and very good spatial resolution. Thanks to the electrochemical probes developed and still used today, measurements are now carried out operationally by many meteorological services. They



FIGURE 6.13: Left: U.S. postage stamp depicting the *Explorer II* balloon. Right: Albert W. Stevens and Orvil A. Anderson in front of the gondola before takeoff. The two aeronauts set a new record on November 11, 1935, reaching an altitude of 72,395 feet.

also use Dobson or Brewer[233] spectrophotometers to determine ozone column values, seasonal variations, and daily variations.

Rocket Measurements

During the Second World War, as mentioned in the previous chapter, Germany developed the V-2 rocket for military use, capable of reaching altitudes of over 100 km. More than 100 of them were discovered by American troops near the town of Norhausen (Thuringia) and sent to *the White Sands* Military Center in New Mexico, where they were modified and adapted to the needs of space exploration. The use of rockets, a challenging technological tool, revolutionized research in the United States. The rocket was an ideal platform for measuring ozone concentrations at altitudes beyond the reach of the large balloons used in

[233] The Brewer Spectrophotometer measures solar ultraviolet and visible, radiation. From the differential absorption of select wavelengths in the UV-B portion of the spectrum, the columns of ozone and sulfur dioxide can be inferred. The instrument was developed in the 1970's by the British-Canadian atmospheric physicist, Alan Brewer together with scientists from Environment Canada. It became operational in the early 1980s.

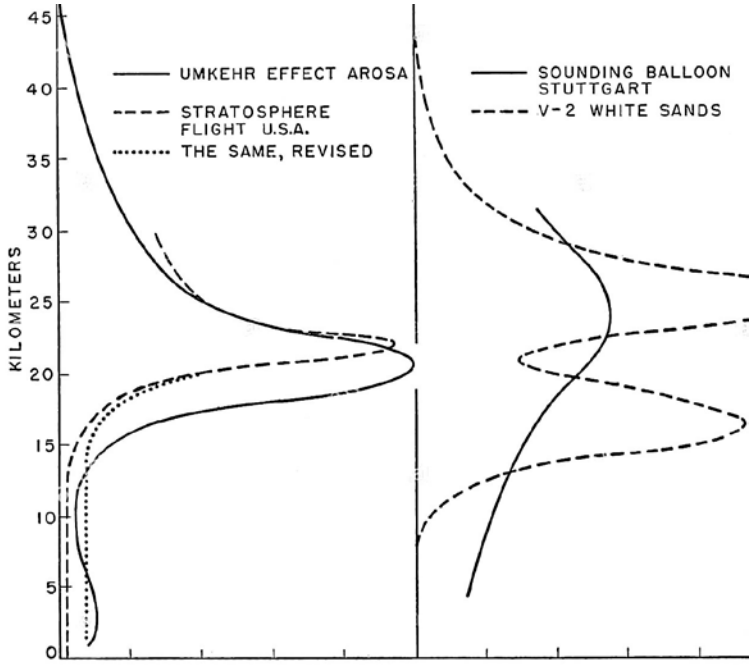


FIGURE 6.14: The first measurements of the vertical distribution of ozone. Left: *Umkehr* measurements in Arosa in the early 1930s and a stratospheric flight with two aeronauts in the Explorer II balloon in South Dakota (USA) in November 1935. Right: Measurements from a balloon launched by Regener in Stuttgart in July 1934 and measurements from a V-2 rocket launched from the US base at White Sands, New Mexico. Source: Götz, F.W.P., Ozone in the Atmosphere. *Compendium of Meteorology,* American Meteorological Society, pp. 275-291, 1951.

the 1930s. But getting accurate measurements from a machine that is moving vertically at more than 1 km per second and vibrating as it rises was a real challenge. Some scientists, including Erich's son Victor H. Regener (1934-2006), suggested that instead of taking measurements directly from the rocket, they should use it to launch an ozone probe at the perigee of the rocket's trajectory. Measurements would then be taken as the probe, deployed under a parachute, slowly descends toward the ground.

Other researchers were trying to make measurements from the rocket itself. Francis S. Johnson, J. Dewit Purcell, and Richard Tousey of the US Naval Research Laboratory installed a spectrograph in the rocket to detect and record the Sun's ultraviolet radiation at different altitudes. From photographic plates recovered from the debris on the ground, the three scientists determined the vertical distribution of ozone. A first launch on October 23, 1946, showed that the maximum ozone concentration was at an altitude of 23.5 km. In a second experiment on April 2, 1948, this maximum was observed at 18.5 km. A third vertical profile of ozone concentration, this time up to an altitude of 70 km, was obtained on June 14, 1949, by a small Aerobee rocket manufactured in the USA. In the 1960s, the ARCAS (American Sounding System) rocket was used to drop chemical probes developed by Victor Regener from an altitude of 50 km.

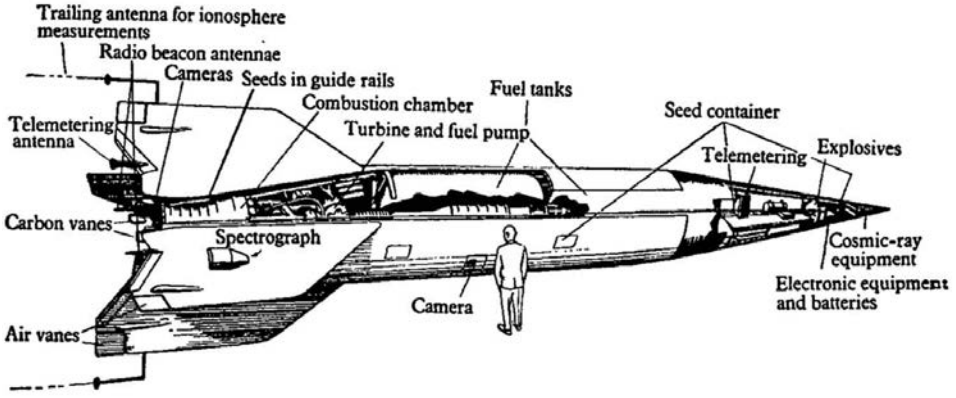


FIGURE 6.15: V-2 rocket confiscated in Germany at the end of World War II and reconfigured in the United States for measurements in the upper atmosphere. The rocket is equipped with a spectrometer to measure the vertical distribution of ozone. Other instruments measure air temperature and pressure. Source: Newell and Siry, 1946 and Goody, 1954.

The Space Age

After the successful launch of Sputnik by the Soviet Union in 1957, American scientific leaders were quick to ask: How could we regain the upper hand in space exploration? What programs could be urgently developed, and what technological and scientific projects should be better funded? Shouldn't the measurement of ozone and other minor constituents present in the upper atmosphere be considered a priority, since some of these species could pose a threat to satellites traveling through the atmosphere?

A first attempt to measure the vertical distribution of ozone in the stratosphere took advantage of *Echo* I, the first American communications satellite launched by NASA on August 12, 1960. This balloon-like spacecraft had a large polyester sphere that reflected electromagnetic waves, especially sunlight. Sekharipuram V. Vankateswaran (1926-2005), a professor at the University of California, Los Angeles, came up with the idea of deriving the vertical distribution of ozone from the intensity of solar radiation reflected by the spacecraft. He showed that the maximum ozone concentration was located at about 25 km altitude, in good agreement with rocket and balloon measurements, but he also observed a second maximum at a higher altitude (55 km), which turned out to be unreal.

A second attempt to observe ozone from space was made two years later by R.D. Rawcliffe of the Aerospace Corporation in El Segundo, California. The method was based on the observation of solar radiation by a radiometer aboard an American Air Force satellite. The ozone concentration as a function of altitude was derived from the attenuation of solar ultraviolet radiation measured when the satellite, moving along a polar orbit, encountered conditions corresponding to sunrise and sunset.

After the successes of the first space missions, it became clear that a more ambitious strategy was needed to observe the chemical composition of the



FIGURE 6.16: *Echo*, the first communications satellite launched on August 12, 1960, is a passive polyester balloon spacecraft developed at NASA's Langley Research Center. It has a diameter of 30 meters and weighs 180 kg. NASA.

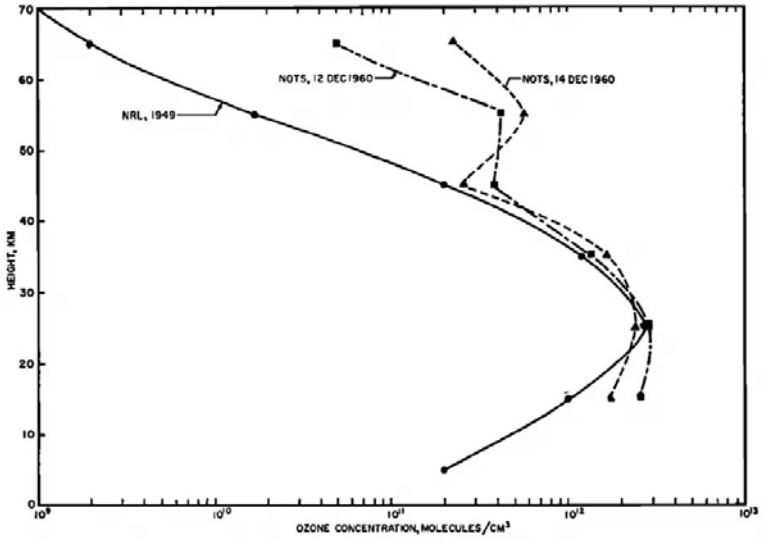


FIGURE 6.17: Vertical profiles of ozone concentration (molecules cm^{-2}) derived in 1960 by Vankateswaran at the University of California, Los Angeles. The concentrations are deduced from photometric measurements over California and compared with those determined from an Arobee rocket launched in June 1949 by the Naval Research Laboratory (NRL).

atmosphere on a continuous, quasi-operational basis. At that time, the Austrian American physicist Siegfried Frederick "Fred" Singer (1924-2020) proposed to determine the ozone content by measuring the solar ultraviolet radiation back-scattered into space by the atmospheric layers. In 1967, an Indian researcher. J. V. Dave and his Canadian colleague Carlton L. Mateer (1926-2011), both working at the National Center for Atmospheric Research (NCAR) in Boulder, Colorado, developed the theoretical foundations of this method. A technique was implemented in several space experiments by the Soviets already in 1964-1965 with the satellite Kosmos 45; then by the US Air Force in 1966; then by a group from the University of Colorado with the OGO-4 satellite in 1967; and by NASA teams with the BUV instrument (Nimbus 4) in 1974 and the SBUV instrument (Nimbus 7) in 1978. The Total Ozone Mapping Spectrometer (TOMS), which measured the ozone column, was also part of the Nimbus 7 satellite.

Other methods of quantifying chemical species in the stratosphere took advantage of the properties of infrared radiation, a technique used by John Gille of NCAR and Jim Russell of NASA-Langley, among others. For example, the Limb Infrared Monitor of the Stratosphere (LIMS) aboard the Nimbus-7 satellite measured thermal infrared emissions from the Earth's limb to determine the concentrations of ozone, water vapor, nitrogen dioxide, and nitric acid in the stratosphere. The Cryogenic Limb Array Etalon Spectrometer (CLAES), part of the Upper Atmosphere Research Satellite (UARS), was based on the same principle. The Halogen Occultation Experiment (HALOE), also on board UARS, used a solar occultation technique in which the instrument observed the Sun both above and through the atmosphere. It measured the absorption of sunlight by atmospheric gases and aerosols to infer the concentration of several chemical species, including ozone, methane, and halogenated species such as hydrogen chloride (HCl).

Finally, measurements in the microwave spectral range provided additional interesting data. For example, the Microwave Limb Sounder (MLS), developed by Joe W. Waters at the Jet Propulsion Laboratory in Pasadena, California, measured the radiation emitted by the limb of the Earth's atmosphere to determine the stratospheric concentrations of ozone, water vapor, and chlorine monoxide. The latter radical plays an important role in ozone chemistry and explains the formation of an ozone hole in the Antarctic region during the austral spring.



FIGURE 6.18: John Gille, Jim Russell and Joe Waters.

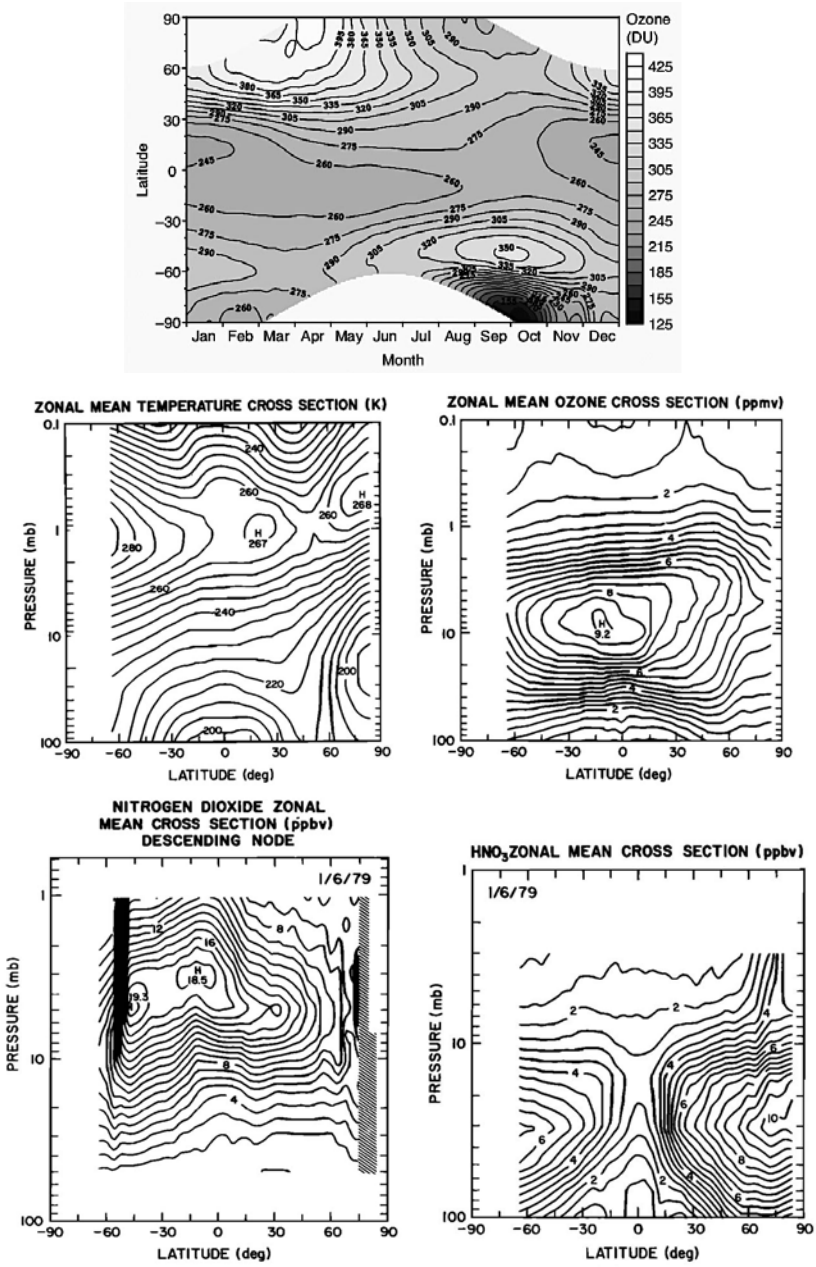


FIGURE 6.19: Illustrative examples of observations of temperature and various chemical species in the stratosphere. Top: Ozone column measured as a function of latitude and season (averages between 1994 and 2003) by the TOMS and GOME instruments. Source: Bodeker *et al. J. Geophys. Res. 106,* 23029-23042, 2001. The other measurements were taken on January 6, 1979 by the LIMS instrument on board the Nimbus 7 satellite. Middle: Zonal mean temperature (in K, left) and relative ozone concentration (ppmv, right). Bottom: Relative concentration of nitrogen dioxide (ppbv, left) and nitric acid (ppbv, right). Source: Gille J. and Russell J.M., *J. Geophys. Res.,* 89, 5125-5140, 1984.

Since then, numerous satellite projects have been implemented by space agencies to observe the Earth and, in particular, the physical and chemical parameters of the atmosphere. Two key initiatives were the Earth Observation System (EOS) project and the European Space Agency's Copernicus Sentinel project. Thanks to the hard work of numerous teams of researchers and technicians, the global distribution and temporal evolution of many atmospheric chemical species are now well known.

Photochemical Ozone Theory

Work done around 1900 showed that the chemistry of ozone is closely related to that of the oxygen atom. However, the mechanisms by which this molecule is formed in the atmosphere remained unknown for a long period of time.

In 1899, Pierre Curie (1859-1906) and Marie Curie (1867-1934), who were studying radioactivity, reported in the *Comptes Rendus de l'Académie des Sciences de Paris* that their collaborator, the chemist Eugène Anatole Demarçay[234] (1852-1903), had made an interesting discovery: "radioactive barium chloride" in contact with ambient air produced an odor like that of ozone. Thus, for Pierre and Marie Curie, ozone resulted from the action of radiation produced by barium, and the "phenomenon was more directly related to radioactivity than to luminosity".

In 1920, Chapman recalled that Erich Regener in Stuttgart had shown that ultraviolet light from the sun had both an *ozonizing* and a *deozonizing* effect, but building on the Curies' work, he mentioned a second possible source of high-altitude ozone[235]:

> "Ozone is always present near radioactive substances, as the Curies first observed; it seems to be produced chiefly by the α-particles. If then aurorae are due to the absorption of α-particles, ozone should be produced, for at 100 km there is still 5 per cent of oxygen [...]. The ozone as formed would diffuse both upwards and downwards-chiefly downwards, owing to the high molecular weight of ozone (half as much again as oxygen). At the same time the ozone would slowly dissociate into oxygen, so that the concentration would be expected to diminish as we recede in either direction from the layer in which it is produced."

Nine years later, at the invitation of Charles Fabry and Gordon Dobson, the first international conference on atmospheric ozone was held in Paris. The aim was to explain why, according to observations, the ozone column was higher in the polar regions than in the tropics. As for the seasonal variation, it seemed to

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[234] Eugène Demarçay French chemist and spectroscopist, collaborator of Pierre and Marie Curie. He is best known for his work in spectroscopy. He confirmed the existence of radium and discovered europium, a rare earth element. He died prematurely at the age of 51, probably as a result of repeated exposure to radium.

[235] Chapman, S., Milne, E.A., The composition, ionization and viscosity of the atmosphere at great heights. *Quarterly Journal of the Royal Meteorological Society, 46*, 357-398, 1920.

CHIMIE. — *Effets chimiques produits par les rayons de Becquerel.* Note de M. P. CURIE et de Mme CURIE, présentée par M. Becquerel.

« Les rayons émis par les sels de baryum radifères très actifs sont capables de transformer l'oxygène en ozone.

» Lorsqu'on conserve le sel radioactif dans un flacon bouché, on perçoit en ouvrant le flacon une odeur d'ozone bien nette. C'est M. Demarçay qui a découvert ce phénomène avec du chlorure de baryum radifère très actif que nous lui avions envoyé, pour ses études spectroscopiques, dans un petit flacon bouché. Le flacon étant ouvert, l'odeur se dissipe incomplètement; pour qu'elle reprenne son intensité primitive, il suffit de refermer le flacon pendant une dizaine de minutes.

» Nous avons vérifié le dégagement d'ozone avec un papier à l'iodure de potassium amidonné qui, placé devant l'ouverture du flacon, se teint légèrement. La teinte est plus foncée si l'on amène du chlorure de baryum radifère au contact du papier, tandis que le chlorure de baryum ordinaire ne produit dans les mêmes conditions aucun effet.

» Les produits radifères nécessaires pour la production de l'ozone sont tous très actifs et tous lumineux. Le phénomène semble plus directement relié à la radioactivité qu'à la luminosité. C'est ainsi qu'un carbonate de radium très lumineux produit moins d'ozone qu'un chlorure de radium bien moins lumineux mais bien plus fortement radioactif.

» La transformation de l'oxygène en ozone nécessite une dépense d'énergie utilisable. La production d'ozone sous l'effet des rayons émis par le radium est donc une preuve que ce rayonnement représente un dégagement continu d'énergie. »

FIGURE 6.20: Excerpt from a paper published by Pierre and Marie Curie and presented by M. Becquerel to the Paris Academy of Sciences in 1899. This article states that oxygen is converted into ozone by the rays emitted by radium.

be of low amplitude in the tropics, but much more pronounced at high latitudes, with a maximum at the end of winter. Did this mean that ozone is formed in the polar regions? What are the mechanisms that explain these phenomena? This was the question. The meeting organized at the Sorbonne in Paris, the first international meeting of ozone specialists, provided an opportunity to summarize what was known, identify outstanding problems, and implement a measurement strategy for the coming years. Determining the vertical distribution of stratospheric ozone concentration was certainly a priority, and in this respect, Götz's Umkehr method seemed to offer new prospects.

Chapman, who had mentioned the role of the aurora in ozone formation, was invited to explain his point of view. But, against all expectations, he came up with a very different explanation: ozone formation would result from the dissociation of molecular oxygen by ultraviolet solar radiation; the two oxygen atoms (O) thus formed would each recombine with an oxygen molecule (O_2) to form two ozone molecules (O_3). He wrote:

> "The greater ozone content in high latitudes than in low, and, in high latitudes, in spring than in autumn (corresponding to a large increase in ozone

> during winter, when these latitudes receive but little ultraviolet radiation) has led several writers to conclude that corpuscular radiation, rather than ultraviolet, must be the chief source of atmospheric ozone: and that the principal role of ultraviolet radiation, which is most abundant during the summer half year, is to reduce the amount of ozone. But [...], it is possible to reconcile the above facts with the hypothesis that ultraviolet radiation is the sole or main source of ozone; and there is at least one reason for regarding this view as more probable than the other. For, according to Fabry, radiation in the band 1300-1850 Å would be principally absorbed approximately at the same level, about 45 km[236], as that at which the ozone is observed to be abundant. The auroral corpuscular radiation, on the other hand, does not descend below about 90 km, and no particles are known which are so penetrating as to get down to 45 km and be there absorbed. Ozone formed at 90 km would descend to 45 km only very slowly, whether by convective mixing or by steady fall under gravity - in the latter case, the time of descent would be reckoned in years."

In other words, ozone is formed primarily where solar ultraviolet radiation is most intense, i.e., in the tropics and subtropics, not in the polar regions. As for the destruction of ozone, Chapman pointed out that the most likely process is the reaction between the ozone molecule (O_3) and the oxygen atom (O), which re-forms an oxygen molecule. It was later discovered that the O_3 + O reaction is relatively slow and that other chemical mechanisms, unknown at the time, would accelerate the recombination between O and O_3.

In the twenty years following Chapman's development of the 1929 ozone theory, little decisive progress was made. Research activities and exchanges between scientists were slowed by international tensions and armed conflicts affecting several countries around the world. Some researchers attempted to calculate the vertical distribution of ozone by solving the equations representing the chemistry of oxygen compounds. These include Reinhard Mecke (1895-1969) at the University of Heidelberg in Germany, and Oliver R. Wulf (1897-1987) and Lola S. Deming (1902-1986) at the U.S. Department of Agriculture's Bureau of Chemistry and Soils. In 1937, these researchers solved the equations of chemical kinetics and showed for the first time that the height of the ozone maximum was located between 20 and 25 km; this result was in good agreement with measurements made in 1934 from the balloon launched by Regener in Stuttgart. However, the calculated ozone concentrations seemed to be much higher than those observed. Nevertheless, the shape of the calculated vertical profile was in good agreement with observations; Lola Deming and Oliver Wulf must be regarded as the first "atmospheric ozone modelers".

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[236] From his initial studies, Chapman concluded that an ozone layer existed at an altitude of 45 km, which seems to be confirmed by measurements taken at Arosa in Switzerland by Paul Götz using the *Umkehr* effect (see Chapter 6). Subsequent measurements carried out in Spitsbergen using the same experimental method, and theoretical work using more recent laboratory data, show that the ozone layer is actually located around 25 km above sea level.

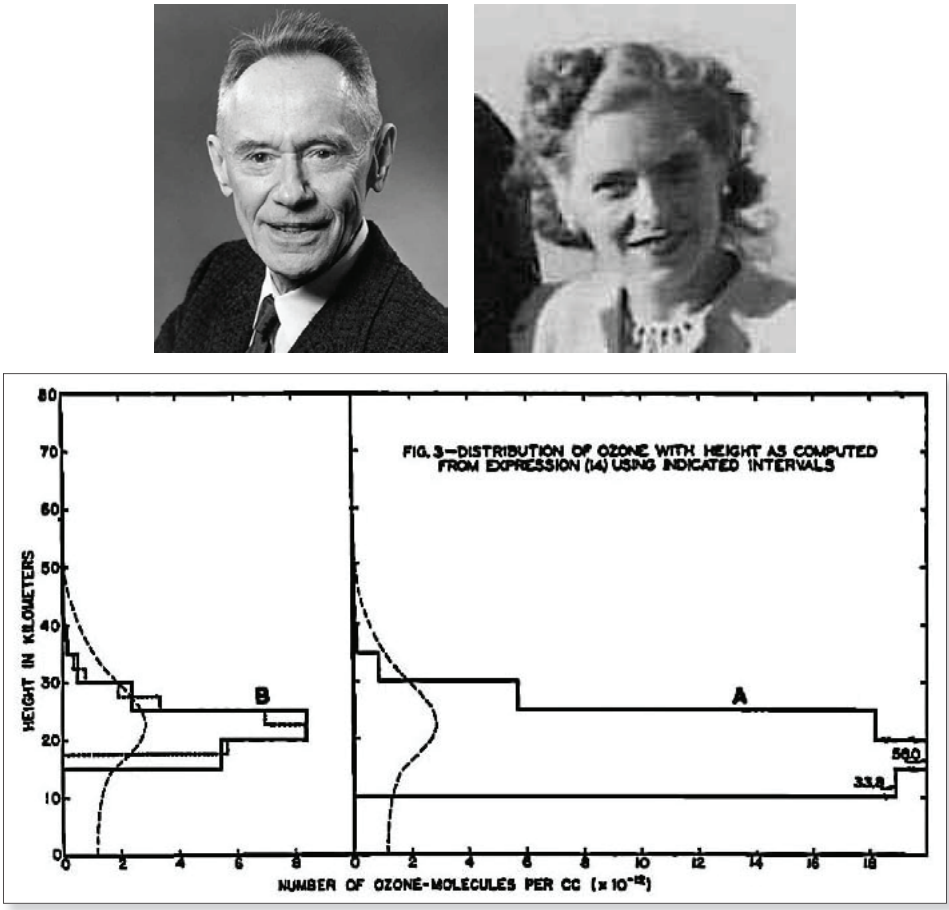


FIGURE 6.21: Top: Oliver Wolf (left) and Lola Deming (right). Bottom: First model of the vertical distribution of ozone (in number of molecules per cubic centimeter) for two assumptions (A and B) on kinetic coefficients that were poorly known at the time, and comparison with the vertical ozone profile determined by Regener in 1934.

The mechanism proposed by Chapman had the merit of simplicity: it involved only oxygen compounds and was based on a very limited number of chemical reactions. In fact, it served as a blueprint for future studies. However, the mechanism had some notable shortcomings. On the one hand, the concentrations calculated based on this simplified chemistry were overestimated in both the stratosphere and the mesosphere; additional ozone-destroying processes had therefore to be considered. On the other hand, the photochemical theory did not explain the existence of the polar ozone maximum. How could these two scientific questions be answered?

The work of David Bates and Marcel Nicolet, mentioned in Chapter 6, provided new insights into the first question in 1950. For these two researchers, working together in Pasadena, California, photodissociation of water vapor in the upper atmosphere produces oxygen radicals (H, OH, HO_2) that react with

atomic oxygen and ozone. This catalytic mechanism leading to ozone destruction is highly effective in the mesosphere and lower thermosphere, and matches calculated and measured concentrations of the ozone molecule only above 50 km. But what about the stratosphere?

In this layer of the atmosphere, despite the studies carried out in the 1950s and 1960s, mechanisms involving hydrogen radicals could not explain the overestimation of ozone by mathematical models below 50 km.

It wasn't until 1970 that Paul Crutzen, then a postdoctoral researcher at Oxford University and later winner of the 1995 Nobel Prize in Chemistry, introduced a second catalytic cycle for the destruction of ozone by nitrogen oxides. When Crutzen published his study based on a photochemical model, nitrogen oxide had not yet been detected in this region of the atmosphere. Four years later, at a conference in Kyoto, Japan, Richard Stolarski (1942-2024) and Ralph Cicerone (1943-2016), two atmospheric scientists at the University of Michigan in Ann Arbor, suggested that the chlorine atom likely present in the stratosphere could also destroy ozone. But it wasn't until a few months later that Mario Molina (1943-2020) and Sherwood "Sherry" Rowland (1927-2012) from the University of California at Irvine published an article in the English journal *Nature* showing that the main source of chlorine in the stratosphere was the production and subsequent emission into the atmosphere of halogenated organic substances: chlorofluorocarbons. For this discovery, the two researchers shared the 1995 Nobel Prize in Chemistry. As we will see in Chapter 10, it is the release of chlorofluorocarbons, produced by the chemical industry and used in various commercial applications, that has been responsible for the formation of a veritable "hole" in the ozone layer over the Antarctic continent during the austral spring since the 1980s.

7
Greenhouse gases

Molecular physics tells us that the most abundant molecules in the Earth's atmosphere-nitrogen (N_2) and oxygen (O_2)-have an important property: they do not absorb infrared radiation. On the other hand, molecules with more than two atoms, such as water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3), all of which are present in relatively small amounts in the atmosphere, do absorb infrared radiation. A considerable number of other chemical species in smaller amounts, such as halocarbons and other organic molecules, often of industrial origin, also have absorption bands in this part of the electromagnetic spectrum. The absorption by these gases of radiation emitted by the Earth's system into space tends to trap some of the energy originally supplied by the Sun, thereby warming the Earth's surface. This phenomenon is called the *greenhouse effect*. Without this natural effect, the Earth would be much colder than it is today, and without liquid water, life in its present form would be impossible. The increase in the atmospheric concentration of gases that absorb infrared radiation is now leading to a warming of our planet[237].

The Discovery of the Greenhouse Effect

Horace Bénédict de Saussure. Geologist and meteorologist Horace Bénédict de Saussure (1740-1799) was born in Conches, near Geneva, into a wealthy patrician family. This Swiss naturalist who descended from Huguenot refugees, was an avid mountaineer and is sometimes considered the father of modern alpinism. At the age of 19, he completed his university studies with a thesis entitled "*Dissertatio physica de igne*" (Dissertation on the Physics of Fire), which

[237] The absorption or emission of a photon by a molecule is associated with a transition between two energy states specific to that molecule. These transitions, and the associated quantum mechanical selection rules, correspond to an emission or absorption spectrum characterized by lines at different wavelengths. Since the 1960s, and thanks to advances in our knowledge of the spectral signatures of chemical species, remote sensing techniques using sensors on board satellites or aircraft, or used on the ground, have provided precise information on atmospheric properties and processes.

dealt with questions related to fire and heat. A passionate mountaineer, a year later, he traveled to Chamonix, France, to admire the imposing Mont Blanc massif from close up. On that occasion, he announced that he was prepared to pay a bounty to the people of the Chamonix Valley who could help him find a way to reach the "roof of Europe", the mythical summit of this natural wonder at an altitude of 4806 meters.

At the age of twenty-two, de Saussure was appointed professor of philosophy at the University of Geneva, which allowed him to carry out an extensive research program in mountain geology, hydrology, glaciology, botany, and meteorology. He made several attempts to climb Mont Blanc but did not reach the summit until August 3, 1787, accompanied by eighteen mountain guides and after two bivouacs during the ascent. Once there, he took a few measurements of pressure, temperature, humidity, and boiling water temperature, but suffered from altitude sickness and immediately returned to Chamonix. At forty-seven, he became the oldest person ever to reach the summit of the mountain range, a record that would not be broken until 1875 by the Marquis de Turenne, who completed the ascent at the age of seventy-two.

To study the properties of the atmosphere, de Saussure then undertook several high-altitude measurement campaigns. In July 1788, he and his son Nicolas-Théodore spent 17 days on the *Col du Géant*, at an altitude of over 3,300 meters, collecting a wealth of scientific data.

During a turbulent period on the brink of the French Revolution, de Saussure took an interest in the political life of Geneva for several years. He aimed to promote a compromise between the patricians, who wanted to preserve their privileges, and the opponents, who demanded political rights. He developed a project to ensure a "solid and lasting peace" for the people of Geneva. However, his activities were brutally interrupted in 1794 by a stroke from which he never fully recovered. De Saussure died ruined five years later.

De Saussure's most important scientific contribution concerned the exchange of heat in nature. To measure the solar energy absorbed by the Earth's surface around the year 1767, de Saussure built an instrument that he called the *helio-thermometer* and took it with him on his various ascents of the Alps. He described the instrument as the precursor of the sun sensor[238]:

> "I made, with planks of pine half an inch thick, a box that was roughly a foot in length and 9 inches wide and high. I lined the inside of all of this box with boards of blackened cork one inch thick, and I closed it with three sheets of very transparent glass placed one above the other, while leaving between them an interval of an inch and a half. When this box was exposed to the sun, its rays passed through the three panes of glass and penetrated to the bottom, where there was a thermometer. A thermometer placed at the bottom of the box and heated by the sun was protected from the action of the outside air." [...]

[238] de Saussure, H.-B., Chapter 35: The cause of the cold that reigns on the mountains, in "*Travels in the Alps*", Vol. 2. Translated from the original text in French, Voyage dans les Alpes, Tome 2, Genève, 1786.

"I took the box to the summit of Crament on 16 July 1774; there I heated it slowly in the sun until the thermometer at the bottom reached 50 degrees."

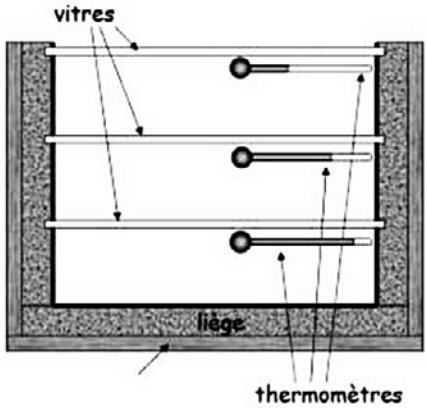


FIGURE 7.1: The heliothermometer conceived and built by de Saussure consists of several "pine boxes" nested inside each other. Thermal insulation between the boxes is provided by layers of cork. The bottom of the boxes is painted black to reduce light reflection. The temperature of the air trapped in each box is measured by mercury thermometers. Source: Bard, E., Greenhouse effect and ice ages: historical perspective / Effet de serre et glaciations, une perspective historique. *Comptes Rendus Geoscience*, 336(7-8), 603-638, 2004.

In some experiments, the temperature measured inside the box reached 128 °R[239] or 160 °C. De Saussure, aware that he was in possession of important scientific information, wrote to the Journal de Paris on April 17, 1784:

"It's a well-known fact, and probably has been for a long time, that a room, a carriage, a bed, are more strongly heated by the sun when its rays pass through glass or closed sashes, than when these same rays enter the same places that are open and unglazed. We even know that the heat is greater in rooms where the windows have double sashes."

Joseph Fourier. The results of this experiment interested the famous French mathematician and physicist Jean-Baptiste Joseph Fourier (1768-1830). Referring to the measurements made by Saussure's helio-thermometer, he introduced the concept of *radiant heat*, which enabled him, in 1824, to describe and explain[240] the heat exchange within the instrument:

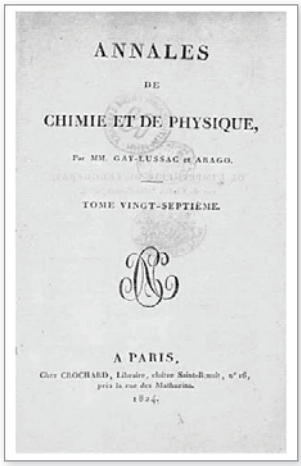
"Just notice that:

- The heat captured by the instrument remains concentrated because it is not immediately dissipated by air exchanges.

[239] Unit of temperature (°R) introduced in 1731 by French entomologist (expert in insects) *René Antoine de Réaumur Ferchault* (1683-1757). The value 0°R corresponds to the freezing point of water, and 80°R to the boiling point of water.

[240] Fourier, J.-B.J., Remarques générales sur les températures du globe terrestre et des espaces planétaires. *Annales de chimie et de physique,* 2e série, XXVII, 136-167, 1824.

- The heat emanating from the Sun has properties that are different from those of obscure heat. The Sun's rays are transmitted to a great extent beyond the glass in all capacities and to the bottom of the box. They heat up the air and the walls that contain it: their heat thus communicated ceases to be luminous; it retains only the common properties of obscure radiant heat. In this state, it cannot freely pass through the glass planes that cover the enclosure; it accumulates steadily in a capacity enveloped by a material that conducts very little, and the temperature rises until the incoming heat is exactly offset by that which dissipates."



ANNALES

DE

CHIMIE ET DE PHYSIQUE,

Par MM. GAY-LUSSAC et ARAGO.

TOME VINGT-SEPTIÈME.

A PARIS,

Chez CROCHARD, Libraire, cloître Saint-Benoît, n° 16, près la rue des Mathurins.

1824.

—

REMARQUES GÉNÉRALES *sur les Températures du globe terrestre et des espaces planétaires.*

PAR M. FOURIER.

LA question des températures terrestres, l'une des plus remarquables et des plus difficiles de toute la philosophie naturelle, se compose d'élémens assez divers qui doivent être considérés sous un point de vue général. J'ai pensé qu'il serait utile de réunir dans un seul écrit les conséquences principales de cette théorie; les détails analytiques que l'on omet ici se trouvent dans les ouvrages que j'ai déjà publiés. J'ai desiré surtout présenter aux physiciens, dans un tableau peu étendu, l'en-

FIGURE 7.2: The first theory of the greenhouse effect published by Fourier in 1824.

Drawing a parallel between the windows of Saussure's box and the Earth's atmosphere, Fourier added that

> "It is in this way that the temperature is increased by the interposition of the atmosphere, because the heat finds less obstacle to penetrate the air, being in the state of light, than it finds to pass back into the air when it is converted into obscure heat."

Fourier had just shed light on the processes that define what is now known as *the greenhouse effect*: visible solar radiation passes through the atmosphere unattenuated and is partially absorbed by the Earth's surface. This surface then emits "dark heat", i.e., infrared radiation, into space. The existence of this



FIGURE 7.3: Jean-Baptiste Joseph Fourier.

radiation, invisible to the human eye, had been demonstrated twenty years earlier by Sir Friedrich Wilhelm Herschel (1738-1822), astronomer to the King of England and a native of the Electorate of Hanover. The atmosphere, by retaining a significant portion of this infrared radiation, limits the loss of energy to space and thus warms the Earth's system. It acts as a blanket around the Earth, preventing heat from being lost to space.

Fourier played a major role in developing the mathematical methods needed to analyze physical phenomena. Throughout his career, he was interested in the propagation of heat in solid media, which gave him the opportunity to develop methods for solving differential equations, study diffusion processes, and introduce the *Fourier transform*, which represents any function by the superposition of periodic functions characterized by different frequencies. This work provoked criticism and disagreement from certain members of the Académie. In 1807, when Fourier submitted his first dissertation on the theory of heat, the venerable institution urged Fourier to revise and perfect his work. The Academy, interested in questions concerning the propagation of heat, made this topic the subject of the *Grand Prix de Mathématiques* to be awarded in 1812. Fourier entered the competition and won the prize. But things weren't quite that simple, as the Académie's perpetual secretary, François Arago, testified in his *historical eulogy* of Fourier, delivered on November 18, 1833:

> "The Académie's positive verdict was qualified by a few limitations. The illustrious commissioners of the prize, Laplace, Lagrange, and Legendre, while proclaiming the novelty and importance of the subject, and declaring that the true differential equations of heat propagation had finally been found, said that they saw difficulties in the author's approach. They added that his means of integration left something to be desired, even on the side of rigor, without, however, supporting their opinion with any kind of development."

It is likely that the Academy commissioners' reservations, without much scientific justification, were more an expression of personal hostility toward Fourier. Arago continued:

> "Fourier never agreed with these judgments. At the end of his life, he even showed quite clearly that he considered them unjust, since he had his prize-winning piece printed in our volumes without changing a single word. Nevertheless, he was constantly reminded of the doubts expressed by the commissioners of the Academy. They had already poisoned his sense of triumph. These first impressions, combined with his great susceptibility, explain how Fourier came to view with some displeasure the efforts of the geometers who were trying to perfect his theory. This, gentlemen, is a strange aberration in such an elevated mind! Our colleague must have forgotten that it is not given to anyone to bring a scientific question to its conclusion, and that the great works on the world system by d'Alembert, Clairaut, Euler, Lagrange, and Laplace, while immortalizing their authors, have constantly added new light to Newton's undying glory."

Fourier's work is collected in his masterpiece, a jewel of scientific literature published in 1822 under the title *Théorie analytique de la chaleur*.

Born in Auxerre, France, Fourier was twenty-one when the French Revolution broke out in 1789. A brilliant student, he hesitated between a military career and a religious commitment. He chose the former and enrolled at the *École Royale Militaire* in Auxerre, where he studied mathematics. He was about to take his vows and enter the abbey of Saint-Benoît-sur-Loire, but a decree of the Constituent Assembly of 1789 forbade this practice. He then became involved in several actions advocated by the Revolution, including the surveillance of foreigners and travelers in Auxerre. The government of the time suspected them of counterrevolutionary activities.

The young scientist's political bias got him into real trouble. His conflicts with other revolutionaries led them to call for Fourier's arrest and execution. He escaped this first sentence following the fall of Robespierre, who was guillotined on July 28, 1794. He then joined the École Normale Supérieure to continue his studies. During the Terror, he was again arrested, this time as a terrorist, and only escaped the guillotine thanks to the interventions of Laplace, Lagrange, and Monge, who had noticed him as a brilliant student. Monge nominated him to the *Conseil d'Instruction* on May 9, 1795, and Fourier became Professor at the École Polytechnique in Paris.

On May 19, 1798, Fourier embarked with the mathematician Gaspard Monge, comte de Péluse[241] (1746-1818), and the Savoyard chemist Claude-Louis Berthollet (1748-1822) on a ship of the French fleet that was carrying Napoleon to a destination known only to a privileged few: Egypt. A few months later, an Egyptian Institute was founded in Cairo to welcome intellectuals from the region. After Napoleon's return to France and the surrender of the French troops surrounded by the British navy, Fourier returned to Paris in 1802, where he resumed his position as professor at the École Polytechnique. Shortly thereafter, Napoleon appointed him prefect of Isère. In 1809, he was made a Baron d'Empire. In 1814, after Napoleon abdicated and was exiled to Elba by the Allies, the monarchy was restored, but Fourier remained in office, serving King Louis XVIII[242] (1755-1824). When Napoleon regained power in 1815 after he escaped from Elba, he dismissed Fourier as an "enemy of the people". After some consideration, however, he appointed him *Préfet* of the Rhône Department but stripped him of his functions and even his pension in 1815.

Finally, it should be noted that Fourier never used the term "greenhouse effect" in his scientific writings, probably because this metaphor only imperfectly represents the processes taking place in the atmosphere. The characteristic of a greenhouse is that gases are trapped in a hermetically sealed glass enclosure. In contrast, there is no such enclosure in the atmosphere, and it is the gases themselves that absorb infrared radiation. The origin of the term "greenhouse

[241] Monge, considered the inventor of descriptive geometry, was Minister of the Navy during the French Revolution, and one of the founders in 1794 of the École Normale Supérieure and the École Polytechnique de Paris, of which he became Director.

[242] The reign of Louis XVIII lasted from 1814 to 1824, but was interrupted between March 10, 1815, when Napoleon I returned from his exile on the island of Alba, and July 8, 1915, after Napoleon I was defeated at Waterloo and was forced to return to exile, this time on the island of Saint Helena.

effect" is not known for certain. It is likely that the term was first used in 1907 by the physicist John Henry Poynting[243] (1852-1914) in a text[244] criticizing the work of one of his colleagues:

> "Professor Lowell's paper in the July issue of *Philosophical Magazine* marks an important advance in the evaluation of planetary temperatures, insomuch as he takes into account the effect of planetary atmospheres in a much more detailed way than any previous writer. But it pays hardly any attention to the 'blanketing effect' or, as I prefer to call it, the 'greenhouse effect' of the atmosphere."

Two years later, the brilliant American physicist and chemist Robert Williams Wood[245] (1868-1955), a professor at Johns Hopkins University, published an article entitled "Note on the Theory of the Greenhouse".

Claude Pouillet. In 1838, twelve years after Fourier's publication on the temperature of the terrestrial globe and planetary spaces, the physicist Claude Servais Mathias Pouillet (1790-1868), a professor at the Sorbonne, published a remarkable article in the weekly journal of the Paris Academy of Sciences entitled *Mémoire sur la chaleur solaire et sur les pouvoirs rayonnants et absorbants de l'air atmosphérique, et sur la température de l'espace*[246]. In this study, this former student of the École Normale Supérieure and member of the Académie addressed a number of questions, including "the proportion of heat absorbed by the atmosphere, the quantity of heat received by the Earth from the Sun in the course of a year, the total quantity of heat emitted at any instant by the entire surface of the Sun, the absolute quantity of heat emitted by a body whose surface, temperature, and radiant power are known, and the general conditions of temperature equilibrium of a body protected by a diathermic[247] envelope analogous to the atmosphere".

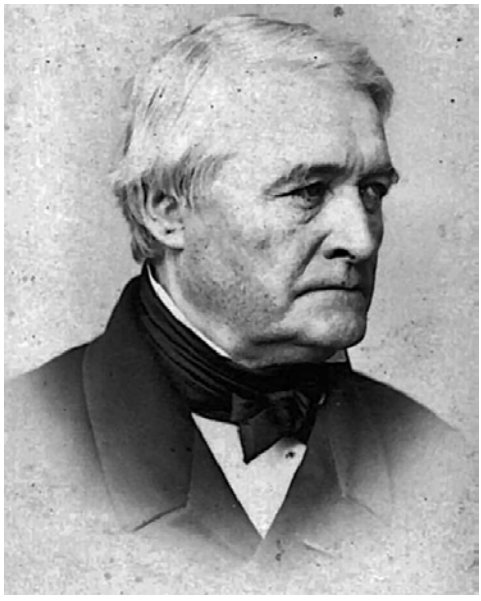


FIGURE 7.4: Claude Servais Mathias Pouillet.

[243] This specialist in electromagnetism is best known for his definition of the "Poynting vector", which determines the direction and intensity of the flow of electromagnetic energy.
[244] Poynting, J.H., *Philosophical Magazine*, *14*(84), 749-760, 1907.
[245] Wood, R.W., *London, Edinburg and Dublin Philosophical Magazine, 17*, 319-320, 1909.
[246] Pouillet, C., *Compte rendus 7*(2), 24-65, 1838.
[247] Diathermic envelope: envelope that lets heat through.

Pouillet presented a mathematical treatment of heat transfer in the atmosphere and estimated for the first time that the solar energy received by the Earth on a surface perpendicular to the path of the rays was 1.7633 calories min^{-1} cm^{-2} or 1228 W m^{-2}, a value 10% lower than the 1367 W m^{-2} measured today.

Pouillet referred to Fourier's work:

> "M. Fourier was, I believe, the first to consider the unequal absorption of the atmosphere as having an influence on the temperature of the ground. He had been led to do so by the fine experiments which de Saussure had made in 1774 on some high peaks in the Alps and in the adjacent plains, in order to compare the relative intensities of solar heat. M. Fourier states precisely one of the principles which I have used to establish the equilibrium equations: only he seems to apply it only to the action of the sun, assuming that this periodic action is the main cause of the decrease in the temperature of the atmosphere."

He clearly distinguished invisible terrestrial radiation from visible solar radiation to explain the "greenhouse effect", pointing out that the atmospheric layer

> "exerts a greater absorption on terrestrial rays than on solar rays."

He added that

> "This difference in action does not result, as is sometimes asserted, from the fact that solar heat is luminous and terrestrial heat is obscure, for to this day everything we know in this respect leads us to believe that there is no such thing as hot light or luminous heat: Rays of heat and light may come from the same source, be emitted at the same time, and coexist in the same ray, but they retain a distinct character, because, on the one hand, they can be separated from each other, and because, on the other hand, there is no example of a ray of heat being transformed into a ray of light, nor of a ray of light proper being transformed into a ray of heat."

In his brief, Pouillet concluded that

> "The decrease of temperature in the atmosphere is not due to the periodic action of the sun, nor to the rising and falling currents. Its real cause lies in the unequal absorbing action of the atmosphere on the heat rays coming from space and on those emitted all around the globe by the surface of the ground or the seas."

In addition to his scientific work, Pouillet, who supported King Louis-Philippe d'Orléans (1773-1850) on the throne from 1830 to 1848, was elected deputy for the Jura region. A year after the fall of the monarchy and the establishment of the Second Republic presided over by Louis-Napoléon Bonaparte, an uprising broke out in Paris. It was directed against the decision of the French president and parliament to organize an expedition to Rome to restore the authority of Pope Pius IX. The latter had fled in the face of the uprising that led to the establishment of the Roman Republic. On June 13, 1849, Parisian insurgents entered the Conservatoire des Arts et Métiers while being pursued by the police. Pouillet, who was both a teacher and a politician, played a mediating role that led to his dismissal two days later by presidential decree. After

the *coup d'État* of December 2, 1851, he refused to swear allegiance to Louis-Napoléon Bonaparte, who proclaimed himself emperor a year later. He was then dismissed from all university functions.

Pouillet is remembered as an exceptional teacher. The chemist Henri Sainte-Claire Deville (1818-1881) said of him in his eulogy in 1868:

> "As Professor at the Sorbonne, M. Pouillet achieved a success that cannot be forgotten. [...] Very sober in his gestures, very simple in his elocution, which he never rushed, he seemed to be conversing with his listeners rather than lecturing them; he gave each of his words such a natural place in the speech that one might have guessed them, had he not spoken them."

Gases that Warm the Planet

Eunice Newton Foote. On the other side of the world, on August 23, 1856, at the annual meeting of the American Association for the Advancement of Science (now known by its initials AAAS) in Albany, New York, an interesting event took place that has been ignored for a century and a half. Eunice Newton Foote (1819-1888) wanted to present the results of her research on the heating of air by solar radiation. She found that air exposed to the Sun's rays heats up more when it contains significant amounts of water vapor and carbon dioxide. At the time, the formation of associations such as the AAAS did not prohibit women from publicly presenting the results of their research; however, the custom was very different. Eunice Newton Foot attended the Albany meeting and asked the Secretary of the Smithsonian Institution, physicist Joseph Henry (1797-1878), to present her work. An article submitted by Foote and published in the American Journal of Science and Arts under the title *"Circumstances affecting the heat of the Sun's rays*" summarized the results of her research. It included the following conclusions

1. The action [of the Sun's rays] increases with the density of the air and is reduced as it becomes more rarified.
2. The action of the Sun's rays was found to be greater in moist than in dry air.
3. The highest effect of the Sun's rays I have found to be in carbonic acid gas.

And she added

> "An atmosphere of that gas would give to our earth a high temperature; and if, as some suppose, at one period of its history, the air had mixed with it a larger proportion than at present, an increased temperature [...] must have necessarily resulted."

To conduct her study and obtain quantitative values, Eunice Newton Foote exposed various gases contained in a glass enclosure to the Sun's rays and measured the resulting heating. The temperature was highest when the enclosure was filled with CO_2. However, Foote did not say whether the gases are heated directly by solar radiation or rather by infrared radiation emitted by the walls of the enclosure. Thus, although she did not refer to the "obscure radiation" invoked



FIGURE 7.5: Eunice Newton Foote.

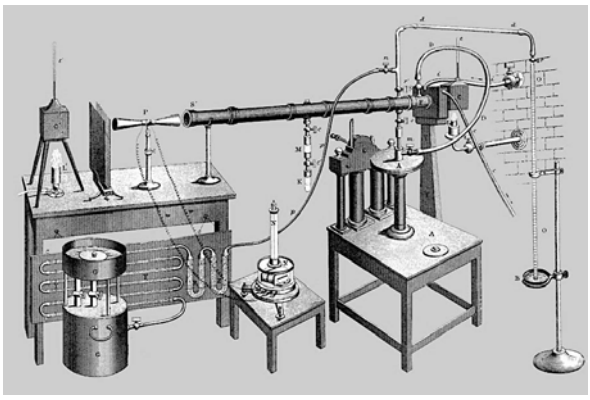
by Fourier in 1824 to introduce the concept of the "greenhouse effect," she did emphasize for the first time the special role of water vapor and carbon dioxide in the Earth's heat balance and in determining atmospheric temperature.

There was no mention of her talk in the minutes of the Albany meeting, but in the 1857 *Annual of Scientific Discovery* (p. 159), David A. Wells stated:

> "Prof. Henry then read a paper by Mrs. Eunice Foote, prefacing it with a few words, to the effect that science was of no country and of no sex. The sphere of woman embraces not only the beautiful and the useful, but the true."

Eunice Newton Foote did not limit herself to research in her laboratory. She was also involved in the women's rights movement and advocated for social reform, particularly the abolition of slavery. She joined the group of activists led by Elizabeth Cady Stanton (1815-1902) in Seneca Falls, New York, where she lived with her husband, Judge Elisha Foote (1809-1883). In 1848, thirteen years before the start of the American Civil War, the "*Declaration of Rights and Sentiments*" was adopted at a convention organized by Cady Stanton in the town. Signed by 68 women, including Eunice, and 32 men, including Elisha, the document called for civil, social, political, and religious rights, including the right to vote for American women.

John Tyndall. Three years after Eunice Newton Foote prepared the paper for the American Association meeting, an Irish engineer, John Tyndall (1820-1893), conducted an important laboratory experiment. He demonstrated that several gases, including carbon dioxide and water vapor, absorb a significant fraction of "dark" radiation, i.e., infrared radiation. He thus made a major contribution to studies attempting to explain the heat balance of the atmosphere. However, Tyndall's publications made no reference to Eunice Newton Foote's earlier work - is this due to ignorance or intention? No one knows. In any case, Tyndall made



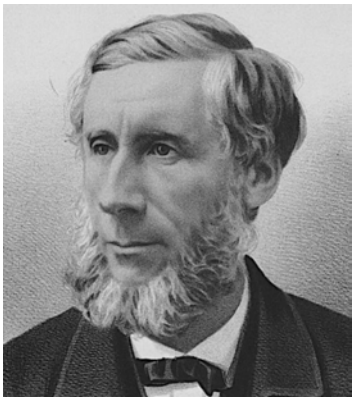


FIGURE 7.6: Left: The experimental system used by John Tyndall to measure the absorption of infrared radiation by various gases. The apparatus consists of a test tube closed at both ends by a layer of rock salt (which allows the radiation to pass through) and into which the gas to be examined is introduced. A thermopile P is placed at one end of the tube. Two copper enclosures C and C′ containing boiling water (both at the same temperature) emit the same radiant energy. Infrared radiation emitted by chamber C, placed at the end of the tube furthest from thermopile P, propagates through the gas contained in the tube before reaching one of the two faces of the thermopile. The radiation emitted by the other enclosure C′ reaches the other side of the thermopile without passing through the gas. A galvanometer labeled N measures the electrical voltage difference between the two sides of the thermopile. This is zero when the tube is empty. On the other hand, in the presence of a gas, part of the radiation passing through the tube is absorbed and the energy intercepted by each of the two faces of the thermopile is different; the galvanometer shows a deviation which is proportional to the amount of energy absorbed by the gas. The gas initially contained in the container is labelled G, and the suction pump is labelled A. The gas is filtered and purified in tubes marked Y and Z, before being injected into the long gas-testing tube. Right: Portrait of John Tyndall.

a clear distinction between the effects of visible radiation from the sun and infrared radiation from the Earth.

Tyndall was born in Leighlinbridge, Ireland, where he began his primary education and a few years later, took up technical drawing. This led to his employment as a draughtsman, first with the Ordnance Survey of Ireland and three years later with the Ordnance Survey of Great Britain, two bodies responsible for topographic mapping and cadastral registration. After signing a petition with several of his colleagues demanding a pay rise and better working conditions, he was dismissed and in 1844 joined a railway company in Lancashire, where he helped develop a new railway line between Halifax and Keighley. In 1847, he became a professor of mathematics at Queenwood College in Hampshire, but with a colleague from the school who became a close friend, he decided to move to Marburg, Germany, to further his education and get closer to what would become his true passion: scientific research. At the time, Germany had acquired an excellent reputation for experimental science, with the presence of such first-rate specialists as the chemist Robert Bunsen (1811-1899), a specialist in the spectroscopy of heated bodies, and the

physicist Heinrich Gustav Magnus (1802-1870), a promoter of experimental physics in Berlin. After completing his doctorate, Tyndall became interested in the magnetic properties of crystals and the relationship between magnetism and molecular structure. His work was noticed by the scientific community, and he was elected a Fellow of the Royal Society in 1852 and Professor of Natural Philosophy at the Royal Institution in 1853[248]. There he met the director of the Institution, Michael Faraday, with whom he worked closely for several years. After Faraday's death in 1867, Tyndall became the new director of the Royal Institution.

Since 1856, the year of his first trip to the Alps, Tyndall had been interested in the processes that govern glacier movement. But in addition to this professional interest, he developed a true passion for the mountains and became an avid mountaineer. He was part of the first group to reach the summit of the Weisshorn in 1861 and participated in one of the first ascents of the Matterhorn in 1868. It's no coincidence that several glaciers (Colorado and Chile) and mountains (California and Tasmania) bear John Tyndall's name.

While working on glaciers, Tyndall became aware of the work of Horace Bénédict de Saussure in the Alps. He learned that the atmosphere seems to retain some of the radiated heat. Fourier's work on heat transfer also caught Tyndall's attention. In 1859, in a paper presented to the Royal Institution, the Irish scientist wrote:

> "These speculations were originated by Fourier; but it was to M. Pouillet's celebrated Memoir, and the recent excellent paper of Mr. Hopkins[249], to which we were indebted for their chief development. It was supposed that the rays from the sun and fixed stars could reach the earth through the atmosphere more easily than the rays emanating from the earth could get back into space. This view required experimental verification."

Tyndall then developed the experimental system that would allow him to accurately determine the absorption rate of different molecules in the air. The instrument he designed consisted of a tube filled with the gas whose absorption properties he wished to determine. A heat source emitting "dark" radiation was placed at one end of the tube. At the other end, a thermo-multiplier[250] built by Macedonio Melloni[251] (1798-1854) at the University of Parma in Italy, measured the radiant energy that passed through the tube. Tyndall observed that the absorption of infrared radiation by individual oxygen, nitrogen, and hydrogen compounds was imperceptible. On the other hand, carbon dioxide absorbs

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[248] Scientific teaching and research organization, founded in 1799 and based in the city of Westminster.

[249] William Hopkins (1793-1866): British geologist and mathematician. He considered that the cooling of the Earth during its geological evolution had no appreciable impact on climate.

[250] Instrument consisting of a thermopile that converts thermal energy into electrical energy and a galvanometer that measures the electrical current produced.

[251] Having taken part in the revolution of 1831, this Italian physicist fled to France. However, he returned to Naples in 1839 to become Director of the Vesuvius Observatory.

1,000 times more than dry air, nitrous oxide absorbs 1,600 times more than its two components, nitrogen and oxygen, and ammonia absorbs 5,500 times more than nitrogen and hydrogen. He deduced that there must be a close relationship between the absorbing properties of matter and the molecular structure of absorbing bodies. He also concluded from his experimental work that water vapor is the most powerful absorber in the Earth's atmosphere; therefore, humidity has a significant effect on the Earth's surface temperature. In a paper delivered to the Royal Institution in 1859[252] Tyndall provided the first scientific definition of the greenhouse effect:

> "The bearing of this experiment upon the action of planetary atmospheres is obvious. The solar heat possesses [...] the power of crossing an atmosphere; but, and when the heat is absorbed by the planet, it is so changed in quality that the rays emanating from the planet cannot get with the same freedom back into space. Thus, the atmosphere admits of the entrance of the solar heat, but checks its exit; and the result is a tendency to accumulate heat at the surface of the planet."

And he ended his text with a curious hypothesis:

> "We have hitherto confined our attention to solar heat; but were the sun abolished, and did stellar heat alone remain, it is possible that an atmosphere which permits advance, and cuts off retreat, might eventually cause such an accumulation of small savings as to render a planet withdrawn entirely from the influence of the sun a warm dwelling-place."

In an article published in 1920[253] Arthur Whitmore Smith, described the British philosopher and physicist, John Tyndall, as

> "a most genial and interesting personality. In him a noble and generous nature was combined with a resolute will and lofty principles. He had a fine regard for the rights and feelings of others, and most of his controversies were in defense of truth and justice."

Tyndall differed from many of his conservative colleagues who were very attached to the precepts of religion; he believed that there should be a clear distinction between science, based on the observation of nature, on the one hand, and religion, which rejected rationalism as the only means of acquiring knowledge, on the other. At a time when his native Ireland was experiencing an independence movement that he believed was led by the Catholic Church, he wrote in The *Times* in 1890 that it would be an "unspeakable crime" to place a people, and especially the non-Catholic minority, under the rule of a "horde of priests".

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[252] Tyndall, J., On the Transmission of Heat of different qualities through Gases of different kinds, Paper presented on June 10, 1859, and reproduced, *in Notices of the Proceedings at the meetings of the members of the Royal Institution of Great Britain with the abstracts delivered at the evening meetings,* Vol. III, 1858-1862, Printed by W. Clowes and Sons, 1862.

[253] Smith, A.W., *The Scientific Monthly, 11*(4), 331-340, 1920.

In 1876, at the age of 55, Tyndall, who had been single, married Louisa Charlotte Hamilton[254] (1845-1940) whom he had met on a trip to the Alps, in 1876. The couple lived happily together on the grounds of the Royal Institution or on vacation in their Alpine chalet, but by the early 1890s Tyndall's health became fragile. He used chloral hydrate to treat his insomnia. One evening in 1893, his wife accidentally administered a fatal overdose. Realizing the desperate situation, Tyndall told Louisa: *"My darling, you have killed your John."* What a terrible story!

One question remained unanswered: what is the exact value of solar energy reaching the Earth? The value of the *solar constant* proposed by Pouillet (1228 W m^{-2}) was the subject of debate and new studies at the end of the nineteenth century. In 1875, the French physicist Jules Violle (1841-1923), a former student of the École Normale Supérieure who taught at the University of Lyon and the Conservatoire des Arts et Métiers in Paris, proposed a value of 1700 W m^{-2} based on measurements he had made during an ascent of Mont Blanc.

Samuel Langley. In the United States, the astronomer Samuel Pierpoint Langley (1834-1906) was interested in the effects of solar radiation on the Earth's climate. A professor of physics and astronomy at the Western University of Pennsylvania (now the University of Pittsburgh) and director of the university's Allegheny Observatory, he built a *bolometer* in 1878 that could measure the electromagnetic energy absorbed by a metal surface after it had been converted into thermal energy. The instrument took advantage of the fact that the electrical resistance of metals is sensitive to temperature. During an expedition to the summit of Mount Whitney (4420 m) in 1881, Langley determined a value of 2140 W m^{-2} for the solar constant. This was almost a factor of two too high. It was nevertheless adopted for several years but later abandoned.

The bolometer Langley built also allowed him to measure the spectral distribution of radiation emitted by various objects in the visible and infrared. These data clearly showed that the spectral signatures of the Sun and room-temperature objects are very different. In fact, the intensity of solar radiation is highest in the visible part of the spectrum (0.6 microns), while that of a body at a temperature of 100 °C, for example, is highest in the infrared region (4.6 microns). Further, the spectral ranges that characterize the two types of radiation are almost completely disjoint. Langley's discovery made it possible to separate the contributions of solar and terrestrial radiation in mathematical climate models. Langley's work thus provided essential information that enabled the various contributions to energy exchange in the atmosphere to be quantified more precisely than in the past. Langley concluded from his research[255] that

> "the Earth's temperature under direct sunshine, even though our atmosphere were present as now, would probably fall to -200 °C, if that atmosphere did not possess the quality of selective absorption."

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[254] Eldest daughter of Lord Claud Hamilton (1813-1884), British Conservative politician and several-time member of the House of Commons.

[255] Langley, S., Professional Papers of the Signal Service No 15, *Researches on solar heat*, p. 123, Washington, 1884.

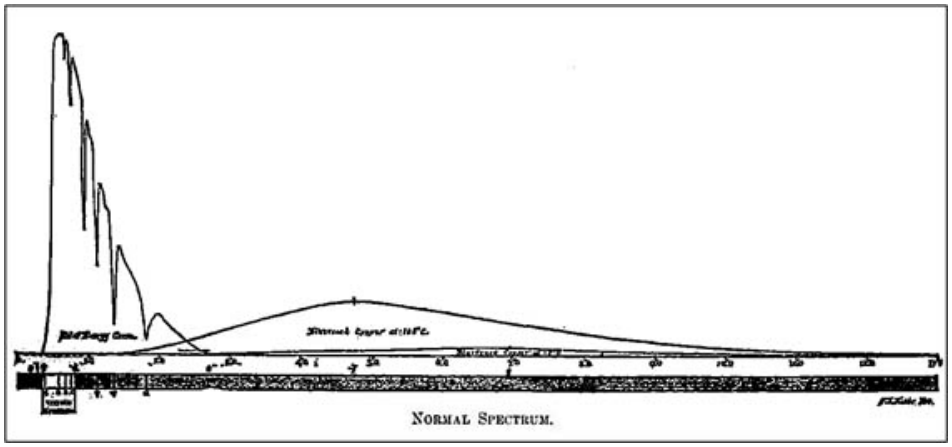


FIGURE 7.7: Langley's (1886) representation of two radiative energy spectra as a function of wavelength expressed in micrometers (μm). The scale varies from 0 to 13 μm in steps of 1 μm. On the left, the solar spectrum observed at ground level with the signature of absorption by various atmospheric gases. The maximum of the solar spectrum is in the visible at around 0.5 μm. On the right, the emission spectrum of a body heated to 100 °C. The maximum intensity is in the infrared at about 5 μm. Source: Langley, S., *Am. Jour. Sci.*, XXXI, 885, 1886.

He thus recognized the important role of the *greenhouse effect*, but his quantitative estimate of this effect was greatly overestimated. He later revised this value after determining that the average effective temperature of the Moon was only -45 °C[256].

Langley was educated at *Boston Latin School*, the oldest school in the United States (founded in 1635); this school prepared many students for prestigious careers and still provides a classical education today. After beginning his career as a draftsman, he traveled to Europe for several months. Upon his return, he entered the Naval Academy in Annapolis, Maryland (1866), and a year later, the Western University (1867). In 1887, he was appointed Secretary of the Smithsonian Institution. In 1876, he was elected to the U.S. Academy of Sciences. Interested in aerodynamics, he thought that he could make heavier-than-air objects fly, so he built model airplanes. One of them, *Langley Aerodrome No. 5*, flew 3,000 feet (900 meters) over the Potomac River. It was the beginning of aviation. In 1903,

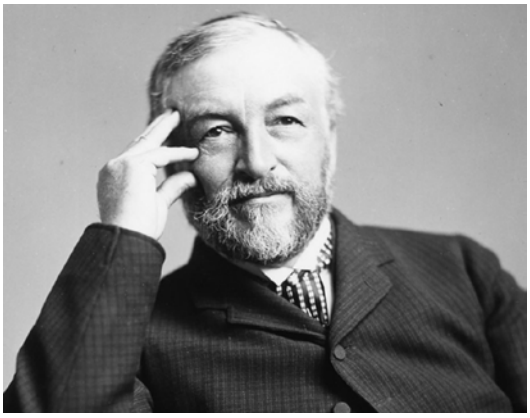


FIGURE 7.8: Samuel Langley.

[256] Langley, S., The temperature of the moon, *Mem. National Academy of Sciences, IV*, 9th mem, p. 193, 1890.

the engineer Charles Matthews Manly (1876-1927) attempted to fly a larger aircraft with an engine and a pilot. On two occasions, the tests were unsuccessful; the planes, launched by catapult from the roof of a boat, immediately fell into the water of the Potomac. The pilot was unharmed both times, but Langley's project was finally abandoned. Nine days after this second failure, on December 17, 1903, brothers Wilbur and Orville Wright made what is considered the first airplane flight, paving the way for the development of aviation.

All the work done in the nineteenth century by the true pioneers of climate science led to an understanding of the mechanisms that characterize the greenhouse effect. By the 1900s, it was well established that solar radiation passes through the atmosphere without much absorption and thus reaches the Earth's surface. On the other hand, *dark heat* - infrared radiation emitted from the surface to space - is largely absorbed by certain gases in the air, particularly water vapor and carbon dioxide. The trapping of this energy causes global warming. Today, it is estimated that without the presence of greenhouse gases, the average temperature of the Earth's surface would be 33 degrees Celsius lower than it is today (15 °C on average).

Carbon Dioxide

The presence of carbon dioxide in the air was discovered by Johan Baptista van Helmont (*gaz sylvestre* or wood gas) and then rediscovered by Joseph Black (*fixed air*), but the atmospheric concentration of this gas was not systematically measured until the nineteenth century. At that time, carbon dioxide (CO_2) in the air was referred to as *carbonic acid*, whereas today the term refers only to the form dissolved in water (H_2CO_3).

Between 1826 and 1830, De Saussure attempted to quantify the amount of "carbonic acid" in the air and its seasonal variation. He obtained values ranging from 200 to 600 parts per million[257] (ppmv), with an average near 480 ppmv. Other measurements were made in France by the famous French chemists Jean-Baptiste Boussingault (1801-1887) and Henri Victor Regnault (1810-1878). The former proposed an average value of 418 ppmv. In Munich, starting in 1855, Max von Pettenkofer (1818-1901), a physician and epidemiologist specializing in public health issues, used a titration technique[258] to determine the concentration of CO_2. Between 1872 and 1880, using a sulfuric acid absorption method, J. A. Reiset[259] carried out a considerable number of measurements at Ecorcheboeuf in northern France and deduced an average CO_2 concentration of

[257] Proportion of molecules of a chemical species relative to the total density of air molecules at a given point in the atmosphere. The "ppmv" (part per million by volume) represents the number of molecules of the species per million molecules of air.

[258] Pettenkofer, M., Über eine Methode, die Kohlensäure in der Atmosphärischen Luft zu bestimmen. *Chem. Soc. J. Tranp., 10*, 292, 1858; and *Journal für praktische Chemie*, *85*, 165, 1862.

[259] Reiset, J., Recherches sur la proportion de l'acide carbonique dans l'air. *Comptes Rendus de l'Académie des Sciences, 90*, 1144-1148, 1880; and *Annales de chimie et de physique. 5*(*26*), 145-221, 1882.

292 ppmv. Reiset's data also showed the existence of a seasonal cycle consistent with that observed today.

On the initiative of the Paris Academy of Sciences, an experiment to measure the CO_2 concentration at altitude was set up in 1875. On April 15 of that year, Joseph Crocé-Spinelli (1845-1875), Henri-Théodore Sivel (1834-1875) and Gaston Tissandier (1843-1899) entered the gondola of the *"Zenith"* balloon. Tissandier was asked to measure the amount of "carbonic acid" by passing ambient air through a tube containing potassium, which retained the CO_2. Crocé-Spinelli was asked to measure water vapor by a spectroscopic method. Sivel, a professional aeronaut, piloted the balloon. The three aeronauts carried three small rubber balloons containing the oxygen they needed to maintain their breathing, but only for one hour. Arriving at an altitude of 8,600 meters, the three men lost consciousness. Tissandier regained consciousness as the balloon descended, but his two companions were unresponsive. They lost their lives. The balloon landed at Ciron in the Indre region. Tessandier wrote after the accident:

> "I felt dizzy, collapsed. The ball descended with frightening speed. I grabbed Sivel and Crocé's arms. 'Sivel! Crocé! Wake up!' I shouted. Sivel and Crocé's faces were blackened, their eyes dull, their mouths gaping and full of blood. I was able to release the anchor at just the right moment. The impact on land was extremely violent. When I stepped ashore, I collapsed; I thought I was going to join my friends in the other world."

In the early 1880s, Charles Achille Müntz[260] (1846-1917) and E. Aubin[261] also used a volumetric method to measure CO_2 in the air, but in this case, they worked on the ground at Vincennes, near Paris. They showed that, in the lower layers of the atmosphere, the CO_2 content is relatively uniform as a function of time; however, they observed slight variations which they attributed to local influences. To estimate the concentration of carbon dioxide at higher altitudes without the need for a balloon flight, the two researchers made observations at the summit of the Pic du Midi in the Pyrenees. Later, they took measurements in the Southern Hemisphere, specifically at Cape Horn at the southern tip of South America. Measurements taken on the Vincennes plain between May and October 1881 showed that the average CO_2 content was about 280 ppmv when the air was of continental and tropical origin, and 277 ppmv when the air was of maritime or polar origin. More than 12,000 measurements were also taken between 1876 and 1910 at the Parc Montsouris Observatory in Paris by Albert Lévy, who became famous for his continuous ozone measurements in the southern

[260] Charles Achille Müntz, Alsatian-born chemist specializing in agricultural and wine-making processes, pupil then assistant to French chemist Jean-Baptiste Boussingault; Director of the Institut National Agronomique, member of the Académie des Sciences de Paris. In addition to his work on the carbon dioxide content of air, he was interested in the role of nitrification as a biological process.

[261] Müntz, A., Aubin, E, Sur les proportions d'acide carbonique dans les hautes régions de l'atmosphère. *Comptes Rendus de l'Académie des Sciences*, *93*, 797-799, 1881; and Recherches sur l'acide carbonique de l'air du Cap Horn et de l'Ocean Atlantique. Recherches sur la constitution chimique de l'atmosphère. Tome 3, Gauthier-Villars, Imprimeur-Libraire. Paris, 1886.

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LES AÉRONAUTES DU « ZÉNITH »

Paris a fait de magnifiques funérailles aux malheureux jeunes gens dont le nom vient d'être inscrit au martyrologe de la navigation aérienne. Paris n'a fait que son devoir.

M. Sivel, ancien capitaine au long cours, était âgé de trente-huit ans. Il avait accompli de nombreuses navigations aériennes, et il était renommé pour son courage et son habileté. A l'époque de la première ascension du *Zénith*, lorsqu'on était inquiet du sort des voyageurs, c'était l'expérience consommée de M. Sivel qui rassurait le personnel scientifique de la Société de navigation aérienne et lui inspirait toute confiance sur l'issue de l'événement. M. Sivel, veuf depuis plusieurs années, laisse une petite fille de cinq ans.

M. CROCÉ-SPINELLI
Mort pendant l'ascension du *Zénith*. — (Phot. Nadar.)

M. GASTON TISSANDIER
Survivant de l'ascension du *Zénith*. — (Phot. Truchelut.)

M. Crocé-Spinelli n'avait que trente et un ans. Il n'était pas marié, mais il était l'unique soutien de son vieux père. Doué d'une intrépidité peu commune, M. Crocé-Spinelli s'était voué corps et âme à ces périlleuses expéditions scientifiques. Collaborateur de la *République française*, il avait apporté à ce journal, le 26 mars au soir, le compte rendu du premier voyage du *Zénith*. — « Il faut, dit-il, que je revoie mon travail, car je l'ai écrit nerveusement et j'ai pu commettre des erreurs. — Vous semblez, en effet, très-fatigué. — Je crois bien, je n'ai pas dormi une minute depuis le jour de l'ascension. » L'ascension avait eu lieu le 23, cela faisait donc trois nuits passées sans sommeil. « — Cela ne fait rien, disait-il, je suis dans un état de fièvre qui ne me permet pas de sentir la fatigue ; et il ajouta : Je me reposerai lorsque nos nouvelles et définitives expériences seront faites. »

M. Gaston Tissandier, le seul qui ait survécu à ce triste voyage, est bien connu dans la science. Rédacteur en chef du journal la *Nature*, il y a écrit de nombreux articles justement estimés. Des trois voyageurs, il était certainement le moins robuste.

Mardi, M. Gaston Tissandier, toujours sous le poids des sentiments qui le suffoquaient, a été, après la cérémonie funèbre, l'objet d'une manifestation affectueuse et sympathique. Un grand nombre de personnes sont venues lui serrer la main et l'ont accompagné jusqu'à sa voiture, à la sortie du cimetière, lui prodiguant tous des témoignages des sentiments qui animent aujourd'hui tout le monde à son égard.

M. SIVEL
Mort pendant l'ascension du *Zénith*. — (Phot. Nadar.)

FIGURE 7.9: Article on three French aeronauts who in 1885 attempted to measure the atmospheric concentration of CO_2 at altitude aboard the "Zenith" balloon.

part of the French capital. Lévy reported that during the period 1877-1878, the average "carbon dioxide" content in the south of Paris was 327 ppmv. However, the Parc Montsouris data are considered by other researchers to be too variable from day to day to be credible[262].

[262] See the article by From, E., Keeling, C.D., Reassessment of the late 19th century atmospheric carbon dioxide variations in the air of western Europe and the British Isles based on unpublished analysis of contemporary air masses by G. S. Callendar. *Tellus, 38B*, 87-105, 1986.

At the University of Liège in Belgium, Bavarian-born botanist and physician Walthère Victor Spring (1848-1911) and his colleague Léon Roland measured an average concentration of 335 ppmv[263]. In a report published in 1886, they noted that the air present in the "cite ardente" (fiery city), located close to blast furnaces and steelworks, was characterized by a "high proportion of carbonic acid, not only relative to the rural air according to M. Reiset, but also relative to the air in Paris". In Gembloux, a small Belgian town 40 km from Brussels and far from industrial zones, Arthur Petermann (1845-1902) and J. Graftiau[264] determined in 1890 and 1892, a carbonic acid content in atmospheric air varying between 275 and 305 ppmv. In 1897 in Belfast, Ireland, Edmund Albert Letts (1852-1918), Professor of Chemistry at Queen's College, and R. F. Blake[265] deduced an average value of 289 ppmv from measurements taken over a 5-month period. Letts, a Fellow of the Royal Society of Edinburgh, was invited to develop a portable measurement system to be taken on board the ship *Discovery.* This ship took Robert Falcon Scott (1868-1912) to Antarctica on his first expedition.

The second half of the nineteenth century was therefore rich in data. Due to the limitations of the instrumentation used, these were highly disparate, typically ranging from 250 to 600 ppmv. However, the careful analysis of this data showed that CO_2 content was highest in air masses originating from industrial and urban areas. Combustion associated with human activity seemed to alter the atmospheric concentration of carbon dioxide. An important question for the study of climate evolution was therefore: what was the pre-industrial atmospheric content of CO_2? It took several decades for this question to be answered.

Another question was: what is the mechanism responsible for the observed seasonal variation in atmospheric CO_2 concentrations? Botanists Horace T. Brown (1848-1925), a Fellow of the Royal Society, and his colleague Ferguson Escombe (1872-1935) provided an answer to this question in the early 1900s. Both were interested in the assimilation of CO_2 by vegetation (the process of photosynthesis) and plant growth. Using an experimental method they had developed based on the absorption of CO_2 by a caustic alkali solution, they analyzed over 90 air samples taken from the Royal Botanic Gardens at Kew (west London) between 1898 and 1901. The average value of the concentrations observed was 294 parts per million by volume (ppmv), but a subsequent analysis, which ignored abnormally high values, showed that the atmospheric CO_2

[263] Spring W., Roland L., Recherches sur les proportions d'acide carbonique contenues dans l'air (Présenté à la Classe des sciences dans la séance du 5 mai 1885), Mémoires couronnés et autres mémoires publiés par l'Académie Royale des Sciences, des Lettres et des Beaux-Arts de Belgique, Tome XXXVII, Bruxelles, Hayez, 94 pp., 1886.

[264] Petermann, A., Graftiau, J., Recherches sur la composition de l'atmosphère. Première partie: Acide carbonique contenu dans l'air atmosphérique, Académie Royale des Sciences, des Lettres et des Beaux-Arts de Belgique. *Mémoires couronnés et autres Mémoires, 47*, 3-77, 1892. Petermann was the director and J. Gaftiau was the head of chemical work at the Gembloux state agronomic station.

[265] Letts, E.A., Blake, R.F., The carbonic anhydride of the atmosphere. *Scientific Proceedings of the Royal Dublin Society, IX, Part 2, No 15*, 107-270, 1900.

content at that time was more likely to be 274 ppmv. The two biologists noted that the concentration of carbon dioxide was slightly higher in winter than in summer, which led them to write[266]:

> "The variations in the atmospheric carbon dioxide are small when regarded as absolute amounts, but they assume considerable importance in the light of what we now know about the relation of the partial pressure of the carbon dioxide in the air to the actual rate of assimilation by the green organs of plants."

Thus, this work highlighted the influence of carbon exchange between the atmosphere and the continental biosphere and provided fundamental information for understanding the global carbon cycle.

In the 1920s, under the influence of the Ukrainian-Russian ecologist Vladimir Ivanovich Vernadsky (1863-1945), the concept of the biosphere, according to which life is directly linked to the interactions between the atmosphere, hydrosphere, and continental landscapes, developed mainly in Eastern European countries. In 1935, another ecological theorist, Vladimir Aleksandrov Kostitsin (1883-1963), presented his first description of the oxygen, carbon, and nitrogen cycles in the Earth system[267]. The Russian-born biomathematician emigrated to France in 1928 and joined the *Centre National de la Recherche Scientifique*[268] (CNRS) when it was founded in 1939. There, Kostitzin developed the first mathematical models of global biogeochemical cycles. He also contributed to research on atmospheric carbon dioxide.

Since then, systematic measurements in the atmosphere and the chemical analysis of small air bubbles trapped in polar ice (which constitute true climate archives) have shown that the concentration of CO_2 in the atmosphere, which was about 280 ppm in 1750, reached 420 ppm in 2024. Experimental work, complemented by more comprehensive global carbon cycle models, also made it possible to estimate the sources, losses, and exchange fluxes between the various compartments of the Earth system. Disturbances in these exchanges following the release of anthropogenic quantities of CO_2 into the atmosphere through the burning of fossil fuels were also estimated. Studies of the carbon cycle are essential for estimating the response of the climate system to human activities. We will return to this issue in Chapter 11.

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[266] Brown, H.T., Escombe, F., On the variations in the amount of carbon dioxide in the air of Kew during the years 1898-1901. *Proceedings of the Royal Society, 76*, 118-121, 1905.

[267] See: Kostitzin, V.A., *Évolution de l'atmosphère, circulation organique, époques glaciaires*, Hermann, Paris, 1935.

[268] The Centre National de la Recherche Scientifique (National Center for Scientific Research) was created on October 19, 1939, following a campaign to mobilize support for research by Nobel Prize-winning physicist Jean Perrin (1870-1942), Under-Secretary of State for Research, with the backing of Jean Zay (1904-1944), Minister of National Education and Fine Arts. Zay was assassinated by the Vichy militia supporting Marshal Pétain during the Second World War.

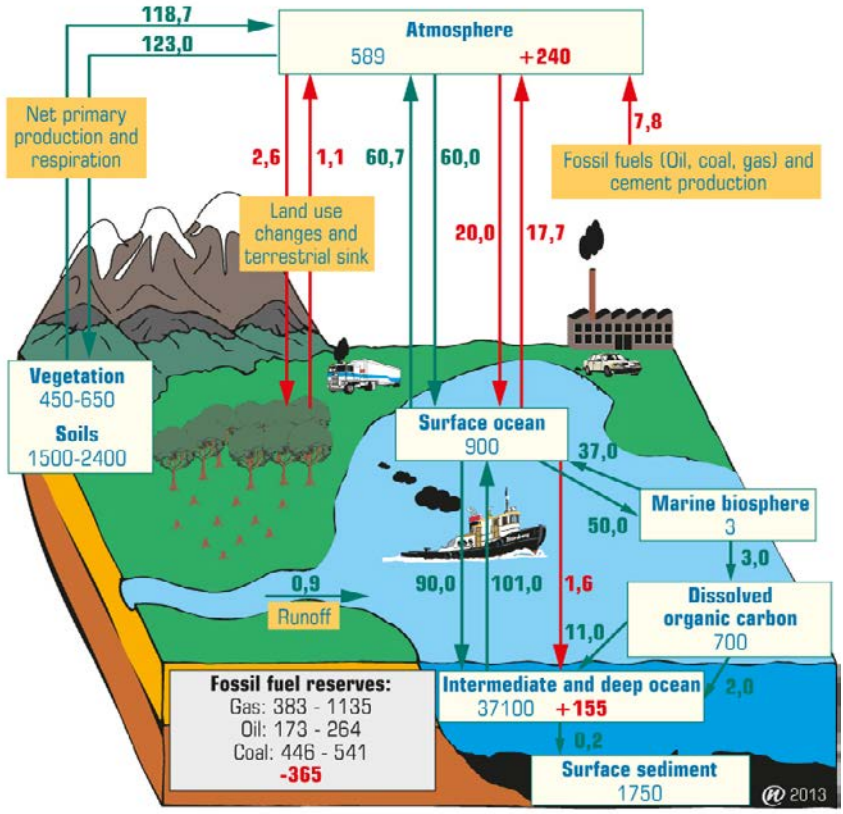


FIGURE 7.10: Global carbon cycle. Carbon stocks in different compartments of the Earth system, expressed in gigatons (Gt) of carbon, are shown in the boxes in the figure. The value of exchange fluxes between compartments, expressed in gigatons of carbon per year, is shown along the arrows. Values in red correspond to perturbations due to human activities. 1 Gt of carbon corresponds to 3.67 Gt of CO_2. Source: Max Planck Institute for Meteorology.

Methane

As is often the case in science, methane was discovered by accident. In the fall of 1776, a young engineer and physicist from Como, Italy, Count Alessandro Giuseppe Antonio Anastasio Volta (1745-1827), known for his invention of the electric battery, visited an illustrious agronomist, Teresa Castiglioni (1750-1821), who lived in Angera, a small town on Lake Maggiore. A year earlier, Volta had been appointed teacher at the public school in Como by Count Karl Joseph von Firmian (1716-1782), an Austrian nobleman who represented the Austro-Hungarian Empire in Lombardy. On this excursion during his school vacation, he noticed the sudden appearance of a blue luminosity overhanging the marshy waters near the island of Partegora. A few months earlier, his friend, Father Carlo Giuseppe Campi, had asked Volta to explain the presence of will-o'-the-wisps seen over a bend in the Lambro River.

Volta was intrigued by the phenomenon, and to explain it, used a stick to stir up the silt that had gradually settled to the bottom of the marsh. Gas bubbles appeared, rising to the surface of the water before escaping into the atmosphere. Volta collected the gas and analyzed it in the laboratory. He discovered that the gas, probably produced by the decomposition of living matter, was flammable and named it "*aria infiammabile native delle paludi*"[269]. But it also showed that this gas is different from the combustible gas (hydrogen) obtained by dissolving metal in acid. Marsh gas burns more slowly and produces a brilliant flame. Proud of his discovery, Volta attempted to make a gun in which methane replaced the gunpowder.



FIGURE 7.11: Alessandro Volta.

In 1787, Antoine Lavoisier also studied this gas and named it *"gas hidrogenium carbonatrum"*. However, it wasn't until 1805 that the chemical structure (CH_4) of this component of air was determined by the apothecary Thomas Henry (1734-1816). The name "methane" was proposed in 1866 by August Wilhelm von Hofmann (1818-1892), a German specialist in organic chemistry at the University of Berlin and a former student of Professor Justus von Liebig at the University of Giessen.

In 1808, the British chemist Sir Humphry Davy (1778-1829), who became president of the Royal Society in 1820, noted the presence of this gas in livestock manure. In 1868, the agricultural chemist Jules Reiset (1818-1896) noticed the release of methane while studying the dynamics of nitrogen in manure. In 1898, Armand Gautier (1837-1920), professor of chemistry at the Paris School of Medicine, observed the presence of this gas over marshes. *Biogenic* methane is produced in a variety of anaerobic (low-oxygen) environments, and its origin is primarily microbial.

The presence of *thermogenic* methane was discovered in coal mines; this gas, produced by the slow transformation of plant debris during coal formation and trapped in coal formations for millennia, is released during coal extraction. Its presence was feared by miners because it is the cause of often fatal explosions. Methane was used to light city streets and, during World War II, as a motor fuel to replace gasoline that had become unavailable. Today, city gas and natural gas, used as a major energy source, contain high levels of methane.

A question remained: is atmospheric methane only present in air masses near its sources? Or is it a permanent component of the global atmosphere? The answer was not found until the late 1940s, thanks to the work of Belgian physicist Marcel Migeotte (1912-1992).

[269] Flammable air from marshes.

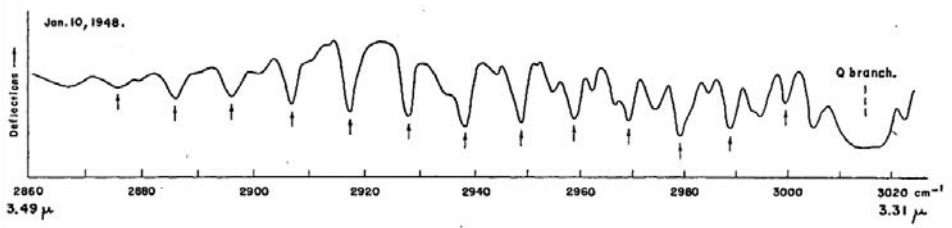


FIG. 1.—The solar spectrum in the 3.4-μ region. Echelette grating: 7200 lines per inch. Slits: 0.2 mm; 0.52 cm⁻¹. The methane lines are indicated by arrows.

FIGURE 7.12: The solar spectrum observed by Migeotte in 1948, with thirteen lines (indicated by arrows) attributed to absorption by atmospheric methane.

Migeotte received his Ph.D. from the University of Liege in 1933. A year later, he moved to Michigan to further his training in infrared radiation, which enabled him to analyze the structure of the solar spectrum. This was the scientific direction he chose when he was hired as an assistant at the *Institut d'Astrophysique in* Cointe, overlooking the Meuse valley in Liège. Migeotte's goal was to create an atlas of the solar spectrum based on the thousands of lines he could detect with the spectrograph he had built. In 1947 and 1948, Migeotte was at the Mendenhall Laboratory at Ohio State University. He had read an article published in 1943 and co-authored by Guy Callendar (1898-1964), which suggested that measuring solar intensity at the Earth's surface at about 3.3 microns could lead to the discovery of new chemical species in the atmosphere. Migeotte, therefore, studied the solar spectrum recorded on January 10, 1948, and noticed the presence of 13 equidistant lines whose wavelengths corresponded exactly to the positions of the lines in the methane absorption spectrum measured in the laboratory. During his visit to the United States, the Belgian scientist discovered the presence of methane in the atmosphere, far from the swampy areas considered by Volta.

Back in Liege, Migeotte obtained permission to install a spectrograph at the Swiss Jungfraujoch station at an altitude of 3,580 meters. Freed from much of the atmosphere at this altitude, he was able to continue his observations of the solar spectrum, greatly reducing the interfering effects of absorption by air molecules. As his spectrograph remained permanently installed at the station, he



FIGURE 7.13: Marcel Migeotte (left) and the Jungfraujoch station in the Swiss Alps (right).

and his collaborators, in particular Rudolph (Rudi) Zander (1938-2015), could follow the temporal evolution of the atmospheric methane concentration. Other chemical species were also detected.

These measurements are crucial for climate change studies because methane is a major contributor to the greenhouse effect. The time-dependent increase in its concentration in the air (0.72 ppmv in 1750 and 1.9 ppmv in 2022) is a source of global warming. We now know that a methane molecule absorbs much more infrared radiation than a carbon dioxide molecule. However, a molecule of methane emitted at ground level remains in the atmosphere for about ten years and disappears faster than a molecule of CO_2. Thus, within 100 years, the greenhouse warming potential of methane molecule[270] due to the greenhouse effect is 25 times greater than that of CO_2. On the other hand, the atmospheric content of methane (1.9 ppmv in 2022) is much lower than that of carbon dioxide (340 ppmv); this is why CO_2 contributes more to the increase in the greenhouse effect than methane, although the latter's contribution is significant and increasing.

Methane is produced mainly by the decomposition of living matter when it is protected from oxygen. Major sources include microbial activity in swamps, agriculture (including livestock digestion) and waste processing, the processing and use of fossil materials (including mining), and the burning of biomass (forest fires, savannah fires). Less intensive sources include emissions from lakes, oceans, termites, and permafrost in Arctic regions. Agricultural development,

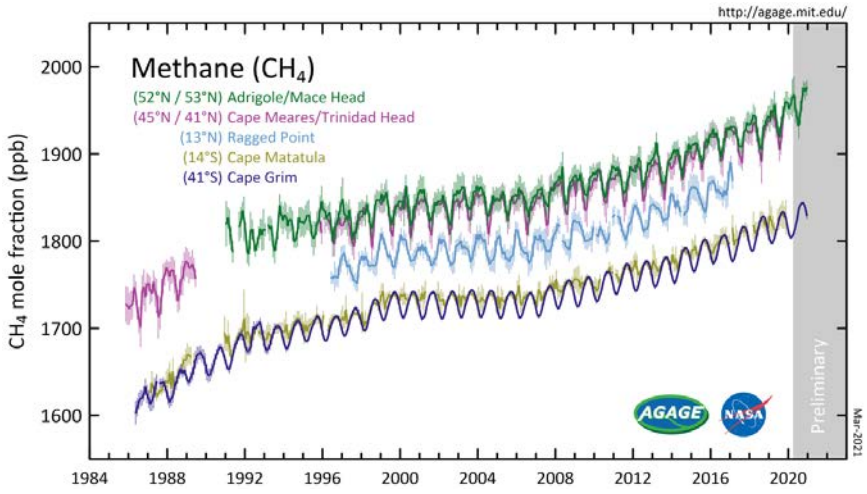


FIGURE 7.14: Mole fraction of methane (CH_4) measured in the near-ground atmosphere as part of the Advanced Global Atmospheric Gases Experiment (AGAGE). Values are expressed as the number of methane molecules per billion molecules of air. Curves refer to observations made at different locations around the world, free of local pollution. Source: Agage.

[270] Global Warming Potential (GWP) is a conversion factor used to compare the relative impact of different greenhouse gases on global warming. It is defined as the warming power of a gas over a given period, compared to the warming power of the same mass of carbon dioxide.

including the expansion of rice paddies in Asia, as well as increased use of fossil fuels and leaks from gas pipelines, are contributing to increases in atmospheric methane. In Arctic regions, the warming of permanently frozen ground (permafrost) could lead to the release of large amounts of methane into the atmosphere. The destruction of this gas results from oxidation processes in the atmosphere and, to a lesser extent, from losses in the soil. With a residence time in the atmosphere of the order of 10-12 years, methane molecules, once emitted at the Earth's surface, disperse into the air and can therefore reach regions far from where the sources are located.

Nitrous Oxide

Nitrous oxide (N_2O), sometimes called laughing gas, is a powerful greenhouse gas produced by certain microorganisms in soils, oceans, estuaries, and coastal areas. The natural production of this gas in soils is enhanced by the application of fertilizers to crops. In addition to the agricultural contribution, smaller anthropogenic sources result from the combustion of fossil fuels and biomass. Human activity is therefore mainly responsible for the increase in atmospheric concentrations of this gas since pre-industrial times (almost 25%).

Nitrous oxide is a very stable molecule in the atmosphere with a lifetime of about 120 years. This is long enough for the molecule to enter the stratosphere, where it is eventually destroyed at high altitudes by short-wave ultraviolet solar radiation. The oxidation of N_2O leads to the formation of nitric oxide (NO), an ozone-destroying agent in the upper atmosphere. Stratospheric ozone levels are therefore influenced to some extent by the action of bacteria in soils.

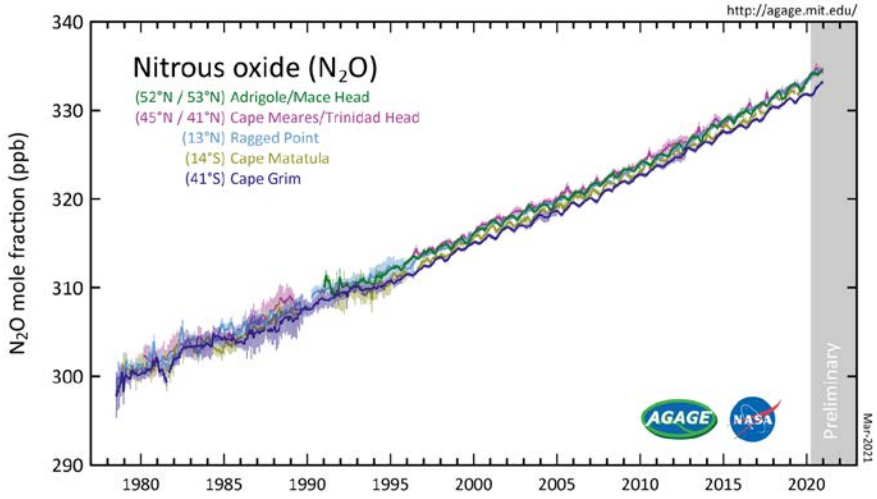


FIGURE 7.15: Mole fraction of nitrous oxide (N_2O) measured in the atmosphere near the ground as part of the Advanced Global Atmospheric Gases Experiment (AGAGE). Values are expressed as the number of nitrous oxide molecules per billion air molecules. The curves refer to observations made in different parts of the world free from local pollution. Source: Agage.

In 1772, English chemist Joseph Priestley synthesized nitrous oxide by soaking iron filings in nitric acid, which he called "*phlogisticated nitrous air*"[271]. It soon became apparent that this gas might have interesting properties. The English physician Thomas Beddoes[272] (1760-1808) claimed that nitrous oxide could cure patients suffering from tuberculosis and other lung diseases. In 1794, he and engineer James Watt (1736-1819), inventor of a new steam engine, published a book on the medical use of "dummy air," and in 1798 opened a sanatorium near Bristol[273]. It housed an enormous machine designed to produce the gas to be inhaled by the patients. The machine operated under the supervision of a young steward, the chemist Humphry Davy. Davy noticed that nitrous oxide had a euphoric analgesic effect on patients who inhaled it and gave it the name *laughing gas*[274].

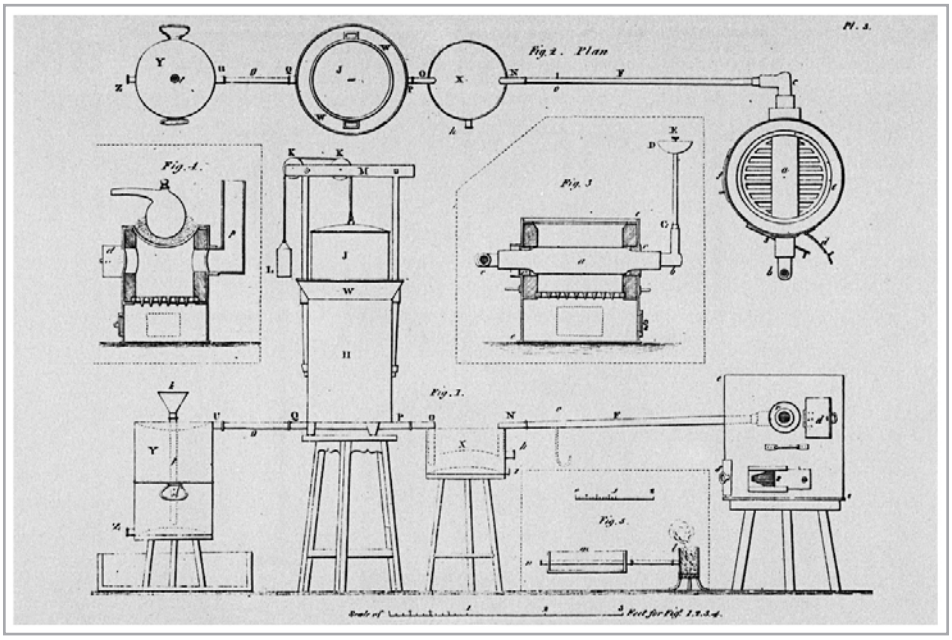


FIGURE 7.16: Thomas Beddoes and James Watt's machine for producing nitrous oxide in large quantities at Hotwells Sanatorium near Bristo. Source: *Considerations on the medicinal use and on the production of factitious airs*; Part I, by Thomas Beddoes, M.D., Part II, by James Watt, engineer; 2nd ed., Bristol, Bulgin & Rosser, for J. Johnson (London), 1795.

[271] The discovery is described in Priestley's *Experiments and Observations on Different Kinds of Air*, published in 1775.

[272] Professor of chemistry at Oxford University from 1788 but had to resign his chair in 1792 because of his sympathies with the French Revolution. Met Lavoisier in Paris in 1786.

[273] The Pneumatic Institution for relieving Diseases by Medical Airs.

[274] "Laughing gas" in English.

In a 2014 essay published by *The Public Domain Review*, Mike Jay recounts how Davy determined this particular property of nitrous oxide[275]:

> "On Boxing Day of 1799 the twenty-year-old chemist Humphry Davy [...] stripped to the waist, placed a thermometer under his armpit and stepped into a sealed box specially designed by the engineer James Watt for the inhalation of gases, into which he requested the physician Dr. Robert Kinglake to release twenty quarts of nitrous oxide every five minutes for as long as he could retain consciousness. The experiment was taking place in the lamp-lit laboratory of the Pneumatic Institution, an ambitious and controversial medical project where the young Davy had been taken on as laboratory assistant [...]
>
> While seated in the box breathing deeply, Davy had felt the effects that had become familiar from his many previous experiments since he had first inhaled the gas earlier that year. The first signature was its curiously benign sweet taste, followed by a gentle pressure in the head as he continued to inhale. Within thirty seconds, the sensation of soft, probing pressure had extended to his chest, and the tips of his fingers and toes. This was accompanied by a vibrant burst of pleasure, and a gradual change in the world around him. Objects became brighter and clearer, and the space in the cramped box seemed to expand and take on unfamiliar dimensions.
>
> Now, under the influence of the largest dose of nitrous oxide anyone had ever taken, these effects were intensified to levels he could not have imagined. His hearing became fantastically acute, allowing him to distinguish every sound in the room and seemingly from far beyond: a vast and distant hum, perhaps the vibration of the universe itself. In his field of vision, the objects around him were teasing themselves apart into shining packets of light and energy. He was rising effortlessly into new worlds whose existence he had never suspected. Somehow, the whole experience was irresistibly funny: he had 'a great disposition to laugh', as all his senses competed to exercise their newfound freedom to its limit.
>
> Now the gas took Davy to a dimension he had not previously visited. Objects became dazzling in their intensity, sounds were amplified into a cacophony that echoed through infinite space, the thrillings in his limbs seemed to effervesce and overflow; and then, suddenly, he 'lost all connection with external things'. [...] Words, images and ideas jumbled together 'in such a manner, as to produce perceptions totally novel': he was no longer in the laboratory, but 'in a world of newly connected and modified ideas', where he could theorise without limits and make new discoveries at will.
>
> After an eternity he was brought back to earth by the sensation of Dr. Kinglake removing the breathing-tube from his mouth; the outside world

[275] Jay, M., *O Excellent Air Bag, Humphry Davy and nitrous oxide*, The Public Domain Review, August 6, 2014. See also the two books: Adam, G. (ed.). *Oh Excellent Air Bag: Under the influence of nitrous oxide, 1799-1920*, PDR Press, 146 pp, 2016, and Jay, M. *The Atmosphere of Heaven*, Yale University Press, London and New Haven, 294 pp., 2009.

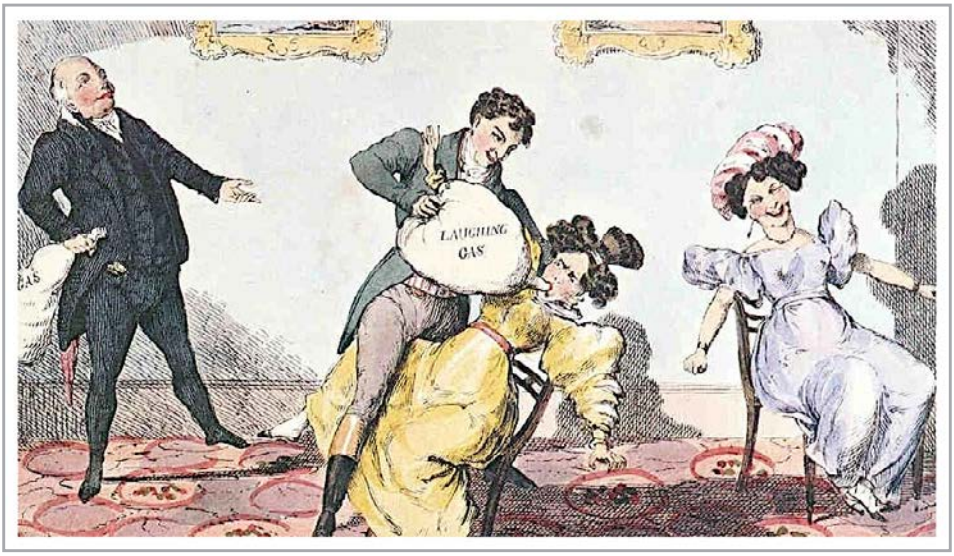


FIGURE 7.17: Satirical 1830 image showing chemist Humphry Davy administering "laughing gas" to a woman as Sir Benjamin Thompson, Earl of Rumford and Davy's friend, looks on.

> seeped back into his 'semi-delirious trance' and, as the energy returned to his limbs, he began to pace around the room. Yet a part of him was still present in the dimension of mind that had swallowed him whole, and he struggled for the words to capture it. [...] 'Nothing exists but thoughts!', he blurted. 'The world is composed of impressions, ideas, pleasures and pains!' "

From 1799, the availability of cylinders of nitrous oxide gave the British bourgeoisie the opportunity to organize "nitrous oxide parties", which became very fashionable for several years. In 1844, the American dentist Horace Wells (1815-1848), who had learned of the beneficial effects of the gas, asked one of his colleagues to extract a tooth after inhaling a volume of nitrous oxide. Feeling no pain, Wells successfully tried the same procedure on twelve patients. He promoted his new technique, which was adopted by many dentists. However, his health deteriorated, and after leaving his family, he fled alone to Manhattan, where he became addicted to drugs. The ether and chloroform he consumed in large quantities caused him to lose his mind, and in January 1848, he was imprisoned for spraying sulfuric acid on two New York prostitutes. Three days later, at the age of 33, he committed suicide in his cell, unaware that he had just been honored by the Paris Medical Society for introducing anesthesia to dentistry. Nitrous oxide would become widely used for mild anesthesia, improving the comfort of even the most anxious patients.

It wasn't until 1939 that the presence of nitrous oxide in the atmosphere was detected. The discovery was made by the American astronomer Arthur Adel (1908-1994). Adel was trying to detect the signature of chemical constituents present in the atmosphere in the infrared spectra of the Sun that he was measuring at the Lowell Observatory in Flagstaff, Arizona. In his experimental

data, he noticed a faint, previously unidentified absorption band at a wavelength of 7.77 microns. He identified this band by comparing the observed atmospheric spectrum with the absorption spectrum of nitrous oxide, an anesthetic that Adel's assistant had obtained from the Flagstaff hospital. Detection was not easy, however, because the N_2O band that appeared in the atmospheric spectrum was partially obscured by a very intense band of water vapor at about 6.3 microns. But Adel was lucky: Flagstaff's atmosphere, located in the northern Arizona desert at an altitude of more than 2,000 meters, contains little water vapor, allowing the N_2O band to appear more clearly. In a more humid atmosphere, the water vapor band would have obscured the signature of this molecule.

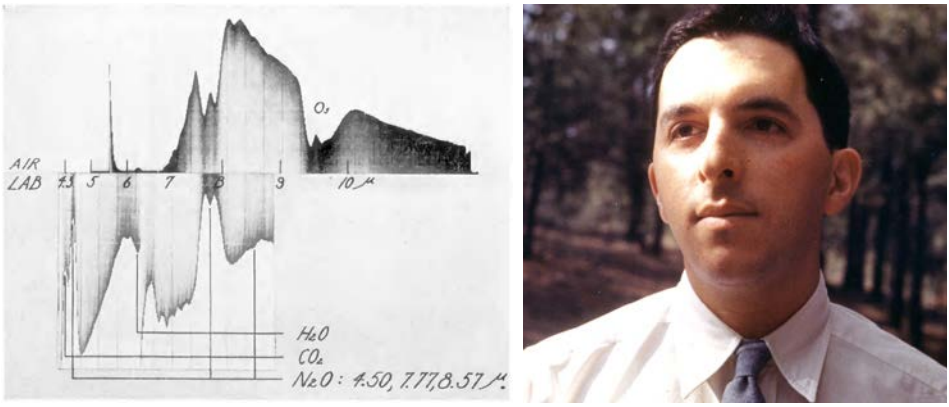


FIGURE 7.18: Left: (Air): Absorption spectrum of solar radiation in the infrared; (Lab): Absorption spectrum of a sample containing nitrous oxide. Note the N_2O band at 7.778 microns in both spectra. Right: Astronomer Arthur Adel.

In the late 1940s, observations of the absorption of solar radiation by spectrographs onboard aircraft confirmed the presence of nitrous oxide in the atmosphere. The N_2O molecule was also detected in the lower layers of the atmosphere and in air trapped in soils. This led Adel to believe that the N_2O molecule, like the nitrogen molecule N_2, is produced by the decomposition of nitrogen compounds such as nitrates by microorganisms in soils. Thus, in addition to its importance in the greenhouse effect, nitrous oxide plays a significant role in the biogeochemical nitrogen cycle, and its presence in the Earth system is intimately linked to the existence of life on Earth.

In 1967, in Belfast, Northern Ireland, David Bates and Paul Byron Hays presented their first analysis of the processes that determine the global balance of nitrous oxide in the Earth's atmosphere. They showed that the main destruction of N_2O is the photolysis of the molecule by ultraviolet solar radiation. Assuming that this destruction is offset by emissions due to the activity of microorganisms in soils, they estimated that the average emission flux of this chemical must be of the order of 10 Tg-N per year[276]. They also indicated that the molar fraction

[276] The emission of nitrous oxide is expressed here as the mass of nitrogen N (rather the mass of N_2O) released to the atmosphere.

of N_2O in soil was close to 250 ppbv. The latter has since increased as a result of human activities, particularly the use of fertilizers in agriculture.

The climate impact of the temporal increase in atmospheric N_2O concentration is substantial. For example, over a 100-year time horizon and on a single molecule basis, the global warming potential of this atmospheric compound is 265 times greater than that of CO_2. However, because the concentration of nitrous oxide in the air is a thousand times lower than that of CO_2, the contribution of N_2O to the greenhouse effect is three times less than that of CO_2 and less than that of methane and water vapor.

Water Vapor

As early as the mid-nineteenth century, Tyndall's laboratory experiments led him to conclude that the dominant absorption of occult heat (infrared radiation) by the atmosphere was due to water vapor, not carbon dioxide. Although fifty years later, Arrhenius and Chamberlin suggested that CO_2 emitted into the air by industry might prevent a return to the Ice Age due to its absorbing properties, it was later recognized that water vapor is the major trap of infrared radiation in the atmosphere. Two researchers at the National Center for Atmospheric Research, Jeffrey T. Kiehl and Kevin Trenberth, recently calculated[277] that in a cloud-free atmosphere, the total radiative forcing[278] due to the absorption of infrared radiation by greenhouse gases is 125 W m^{-2}. The contribution of water vapor to this warming is 75 W m^{-2} (60%), and that of CO_2 is 32 W m^{-2} (26%). Other greenhouse gases contribute less: 8% from ozone and 6% from methane and nitrous oxide. If the additional effect of clouds is considered, total warming by infrared radiation reaches 155 W m^{-2}.

What is the specific role of water vapor in the greenhouse effect compared to carbon dioxide, methane, and nitrous oxide? On the one hand, the residence time of a water molecule in the air is much shorter than that of the other three greenhouse gases, only a few days, which limits its long-term global warming potential. On the other hand, unlike CO_2, methane, and nitrous oxide, water vapor is not emitted in significant quantities as a result of human activities. Its concentration in the atmosphere is the result of natural evaporation and condensation processes, the intensity of which varies with weather and climate conditions. Thus, as the atmosphere warms, for example, because of increased CO_2 emissions, evaporation intensifies and the atmospheric water vapor content increases, amplifying the initial warming. From a climatic point of view, the presence of water vapor thus introduces a warming amplification mechanism known as *positive feedback*.

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[277] Kiehl, J.T., K.E. Trenberth, Earth's annual global mean energy budget. *Bulletin of the American Meteorological Society, 78*(2), 197-208, 1997.

[278] Radiative forcing is equal to the difference between the emission of infrared radiation at the Earth's surface and the outward emission of the same radiation at the edge of the atmosphere.

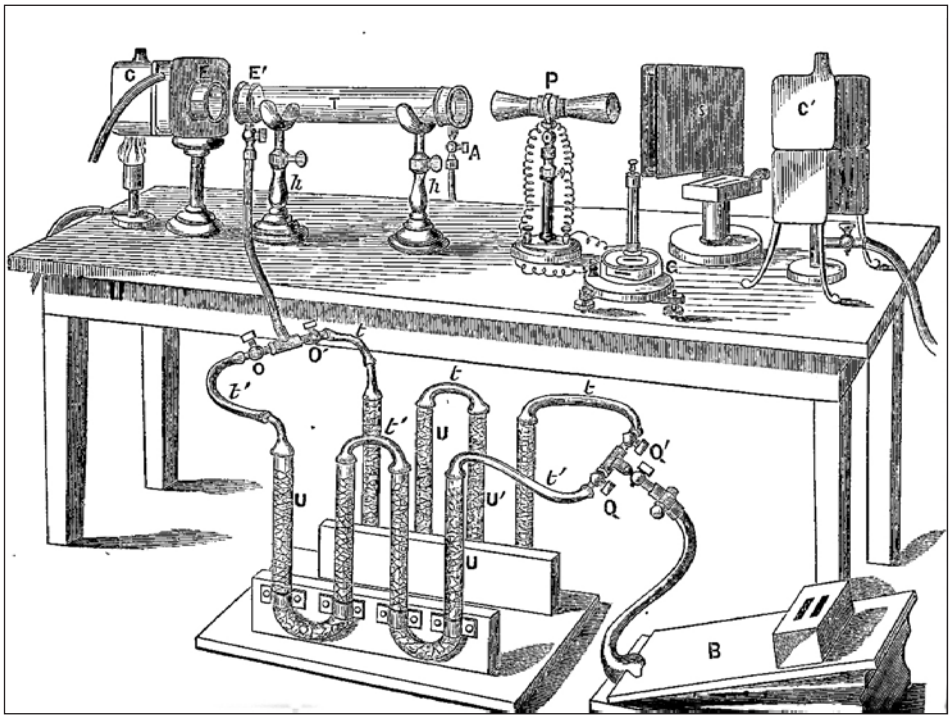
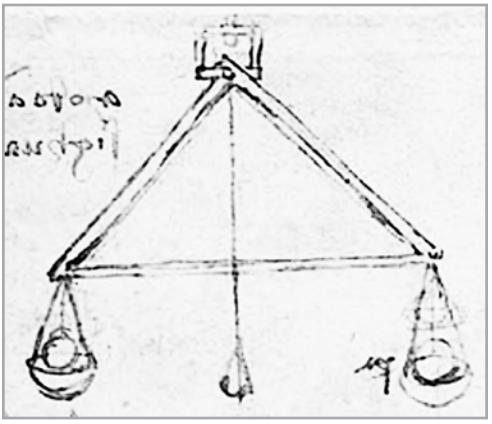


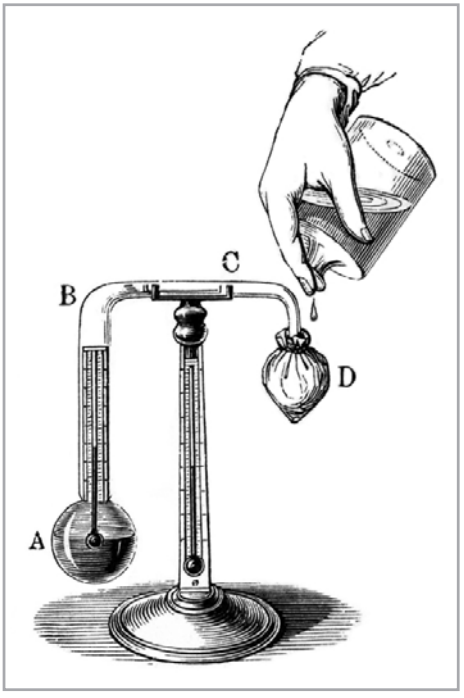
FIGURE 7.19: Tyndall's laboratory apparatus for measuring the absorption of water vapor by "occult heat". The principle of the experiment is as follows: A measurement is made alternately for humidified air and for dried air. The apparatus is similar to that used to measure CO_2 absorption (see Figure 7.6), with a few differences. Air from a rubber enclosure B is pumped into tube T via a pump located beyond point A. Valves Q and Q′ are opened alternately so that the air flows either into tube U, filled with glass fragments moistened with distilled water, or into tube U', filled with glass fragments "moistened" with sulfuric acid. Enclosures C and C′ represent heat sources of equal intensity, and P is a thermopile connected to a galvanometer G. The galvanometer deviation results from the dominance of radiation from source C′ (whose radiation is not absorbed) over that from source C (whose radiation is absorbed by the air in tube T) and therefore represents a measure of absorption by water vapor. Source: *Heat considered as a mode of motion: being a course of twelve lectures delivered at the Royal Institution of Great Britain in the season of 1862* by John Tyndall, F.R.S, Professor of Natural Philosophy in the Royal Institution.

The presence of water vapor in the atmosphere has been known for a very long time: as early as the fourth century BCE, Aristotle referred to it in his work *Meteorologica*. However, accurate measurement of atmospheric water vapor concentration and its temporal variability is difficult to achieve. It is said that in China, during the *Shang* Dynasty (ten centuries BCE), humidity was determined by measuring changes in the mass of a charcoal stick wrapped in a clod of earth. In Europe, a new branch of meteorology, hygrometry, was developed in the fifteenth century to determine the amount of

water vapor in the atmosphere. At that time, the first instruments appeared, known as hygrometers (from the ancient Greek ὑγρός, damp, and μέτρον, to measure) based on the hygroscopic properties (changes in mass, shape, or color) of certain organic substances. To develop his hygrometer, the German Catholic theologian, mathematician and astronomer from the Mosel town of Kues in Germany, Cardinal Nikolaus de Cusa (1401-1464), used wool (1450), Leonardo da Vinci (1452-1519) in Florence used cotton (1481), the Paduan physician Santorio Santorio (1561-1636) used a lead ball suspended from a moisture-sensitive string (1623), English scientist Robert Hooke (1635-1703), Isaac Newton's contemporary and great adversary, used an oatmeal beard (1625), and Swiss geophysicist Horace Benedict de Saussure used human hair (1781). In 1815, French chemist and physicist Gay-Lussac established a relationship between hair hygrometer measurements and the value of relative humidity. In 1819, English chemist John Frederic Daniell (1790-1845) invented a condensation hygrometer, which measured the dew point (the temperature at which water vapor condenses) to determine the relative humidity of the air. The Scottish mathematician and physicist Sir John Leslie (1776-1832) determined the humidity of the air by the difference between the temperatures measured by two thermometers: the first, known as a *dry* thermometer, determined the temperature of the ambient air; the second, known as a *wet* thermometer, derived the temperature of a muslin cloth, permanently soaked in water, which surrounded the instrument's mercury bulb. Evaporation of the water in the muslin requires heat from the immediate environment, so the temperature measured by the second thermometer was lower than that of the first. Evaporation, and therefore the temperature difference between the thermometers, is a function of the relative humidity of the air. It was the German physicist Ernst Ferdinand August (1795-1870) who, in 1825, gave this new instrument the name psychrometer (from the ancient Greek ψυχρὸς, cold, and μέτρον, measurement).

Today, the frost-point hygrometer is commonly used. This instrument consists of a mirror that is gradually cooled until the water vapor in the surrounding air condenses on it. The traces of condensed water are detected by a beam of light reflected from the mirror to an optical detector. The temperature of the mirror, which represents the temperature at which the air is saturated with water vapor, is compared with the ambient temperature to determine the relative humidity of the air. Other methods are based on the molecular properties of water, using the properties of infrared spectrometry and microwave radiometry, which allow measurements to be made from space platforms or from the ground. The absorption of the GPS signal as it passes through the atmospheric layers also allows water vapor to be measured from satellites. The vertical profile of water vapor is also determined from the ground using a beam sent upward by a lidar. Various types of sensors attached to weather balloons launched by meteorological services measure humidity as a function of altitude on a daily basis.





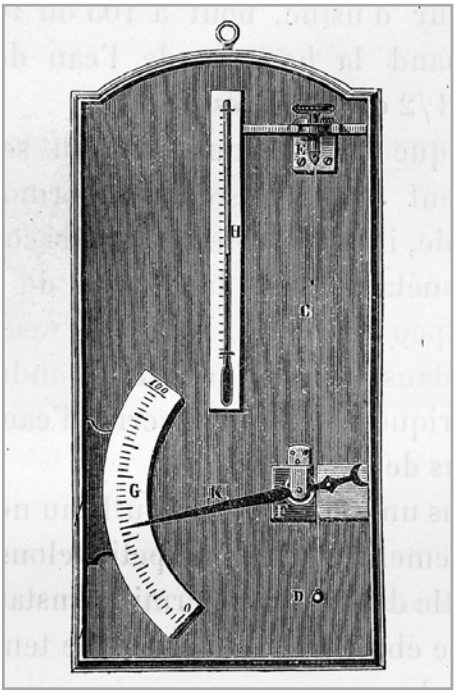


FIGURE 7.20: Above: Drawing of the hygrometer designed by Leonardo da Vinci in 1481, which appears in the corner of a page in his notebooks. Bottom left: Condensation hygrometer invented by John Daniell in 1819. The system consists of two sealed flasks connected by a glass tube (C). The balloon on the left (A) contains ether in which a thermometer is immersed. If ether is poured onto the fabric covering the right-hand flask, the latter cools as the ether soaking the fabric evaporates. This cooling causes the ether vapor trapped in the right-hand flask (D) (under the fabric) to condense. As a result, the vapor pressure in the system drops, and the ether in the left-hand flask begins to evaporate. As a result, the left-hand flask cools until the dew point is reached. At this point, dew is deposited on the outer wall of the left balloon. The temperature value measured by the thermometer inside this balloon is used to determine the humidity of the air. Below right: hair hygrometer designed by Horace Bénédict de Saussure.

Other Greenhouse Gases

While for many years discussions of likely global warming were limited to examining the effects of CO_2 and water vapor, and to a lesser extent methane and nitrous oxide, climatologist Veerabhadran Ramanathan[279] ("Ram") at the National Center for Atmospheric Research reported in 1975 that chlorofluorocarbons, produced by the chemical industry and known for their ability to destroy stratospheric ozone, were also contributing to the greenhouse effect. Their effect on surface temperature would become apparent if the atmospheric concentration of these gases, which are distributed at all latitudes, reached 2 parts per million. A few years later, in 1985, Ramanathan[280], together with his NCAR colleagues Ralph Cicerone and Jeffrey T. Kiehl, and NASA colleague Hanwant B. Singh, showed that the increase in atmospheric greenhouse gases other than CO_2 contributes as much to the greenhouse effect as CO_2. This work has prompted the scientific community to broaden its approach and to quantitatively determine the radiative forcing produced by a large number of molecules present in the air that interact with infrared radiation. These gases contribute to some extent to global warming.

Calculating the Greenhouse Effect

What is the effect of greenhouse gases on the average temperature of the Earth? Does an increase in the atmospheric concentration of these gases, for example as a result of human activity, lead to an increase in this temperature? To answer these questions and to gain a clearer understanding of the mechanisms behind the greenhouse effect, we present a simple and conceptual model of the Earth's climate.

As a first step in defining reference conditions, we assume that the Earth's atmosphere is perfectly transparent to both incident solar radiation (ultraviolet and visible) and terrestrial radiation (infrared) emitted from the Earth's surface. The solar energy intercepted by the Earth has been precisely measured: it is close to 340 W m^{-2}. About 30% of this energy is reflected by the Earth's system (known as the terrestrial albedo) and sent back to space so that the average amount of solar energy stored by the planet is 240 W m^{-2}. The Stefan-Boltzmann law (see Box 7.1) tells us that the energy emitted by the Earth into space is proportional to the temperature of the emitting body raised to the power of four. At equilibrium and on average, the net amount of solar energy absorbed by the Earth should be equal to the terrestrial energy emitted into space. In the absence of absorption processes in the atmosphere, the Earth's

[279] Ramanathan, V., Greenhouse effect due to Chlorofluorocarbons: climatic implications, *Science, 190*(4209), 50-52, 1975.
[280] Ramanathan, V., Cicerone, R.J., Singh, H.B., Kiehl, J.T., Trace gas trends and their potential role in climate change. *Journal of Geophysical Research, 90*(D3), 5547-5566, 1985.

temperature T_e that satisfies this equilibrium is -18 °C, i.e., 33 °C lower than the temperature deduced from observations.

Now consider, as Fourier suggested, that the atmosphere is transparent to incident solar radiation, but includes a layer of gases (known as greenhouse gases) that is *totally* opaque to the infrared radiation emitted by the Earth's surface. This layer itself emits infrared radiation both upwards to space and downwards to the ground. Again, using Stefan-Boltzmann's law (both for surface emissions and for emissions from the absorbing gas layer) and expressing the radiative energy balance at the top of the atmosphere and at the ground, we deduce that the average temperature of the ground is 29 °C. Under the effect of the absorbing gases present in the atmosphere, this temperature is therefore considerably higher than that obtained by omitting the presence of these gases in the atmosphere. It is also higher than observed. We need, therefore to increase the complexity of our model and consider additional processes that we have so far ignored. What are the shortcomings of the simplified model we have used to present the concept of the greenhouse effect?

First, the atmosphere is not completely opaque in the infrared. In fact, the absorption of terrestrial radiation by molecules such as water vapor, carbon dioxide, or methane does not occur at all wavelengths. There are narrow spectral windows that allow a fraction of the radiation to reach the top of the atmosphere and thus be emitted to space. On the other hand, greenhouse gases are not confined to a single layer but are present at all altitudes in the atmosphere, where there are exchanges of radiative energy. Each layer absorbs and re-emits radiation with an intensity that depends on the local temperature of that layer. Finally, we need to revise the assumption that the atmosphere is completely transparent to incoming solar radiation. A fraction of this radiation is absorbed by gases such as ozone. It also interacts with atmospheric dust and clouds, which absorb, scatter, and reflect some of the visible light. To these radiative properties, the exchange of non-radiative energy associated with changes in the state of water (latent energy) and turbulent exchanges (sensible energy) in the planetary boundary layer must be added.

The mathematical models that take these different processes into account are called radiative transfer models. They allow us to determine the temperature at ground level and the vertical temperature profile in the atmosphere, once the chemical composition of the air is known. Their complexity compared to the conceptual models just described (Box 7.1) is due to the detailed formulations used to describe the interactions between ultraviolet, visible, and infrared radiation and the molecules, clouds, and other particles present in the atmosphere.

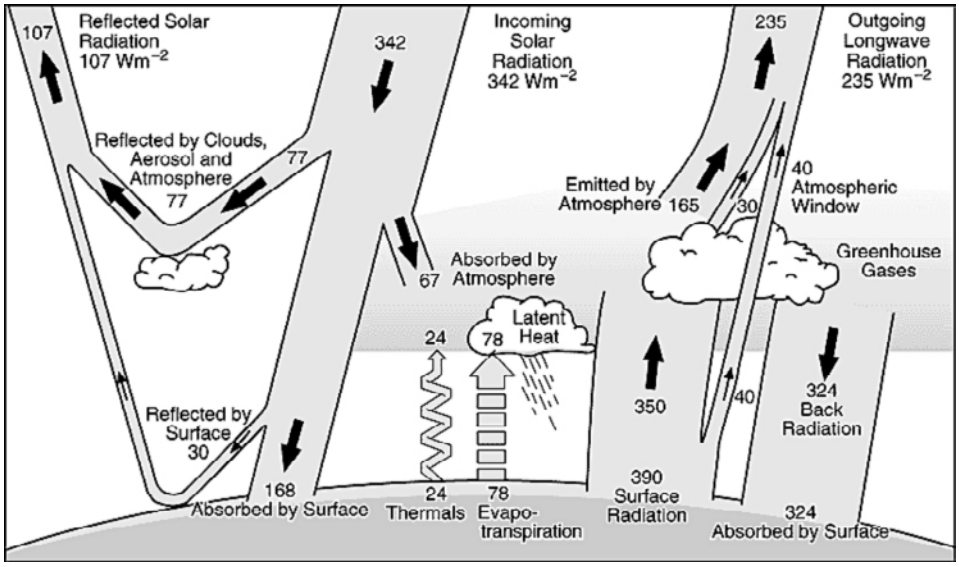


FIGURE 7.21: Schematic representation of the average global energy balance of the Earth as estimated by J. T. Kiehl and K. E. Trenberth (*Bull. Amer. Meteor. Soc.*, **78**, 197-208. 1997). Values expressed in watts per square meter (W m^{-2}) indicate the magnitude of the components of the average global energy balance at the end and beginning of the twentieth century. Of the incident solar radiation, 168 W m^{-2}, or 49%, is absorbed by the Earth's surface, while the rest is either reflected back into space (107 W m^{-2}, or 31%) or absorbed by the atmosphere (67 W m^{-2}, or 20%). This energy is returned to the atmosphere through thermal radiation (390 W m^{-2}), evaporation (78 W m^{-2}), or as sensible heat (24 W m^{-2}). Most of the upward heat flux is absorbed by the atmosphere, which re-emits this infrared radiation both upward and downward. Some of this radiation is lost to space (235 W m^{-2} energy loss), while some (324 W m^{-2}) remains trapped in the Earth system. It is estimated that the slight imbalance between the sunlight absorbed by the terrestrial system and the thermal radiation emitted to space is close to 0.6 W m^{-2}. This accumulation of heat by the Earth, mainly in the oceans, leads to global warming.

Box 7.1. Simplified calculation of the Earth's average temperature

On average, the Earth intercepts 340 W m^{-2} of solar energy. About one third of this energy, or 102 W m^{-2}, is reflected to space by the Earth system, and the albedo α is therefore 0.3. The difference of 238 W m^{-2} is absorbed by the planetary system. The Earth, assimilated to a black body, emits infrared radiation; the energy emitted E is determined as a function of the equivalent temperature of the black body T_e by Stefan-Boltzmann's law:

$$E = \sigma T_e^4$$

where the constant $\sigma = 5.67 \times 10^{-8}$ W m^{-2} K^{-4}.

The Earth's temperature is determined by expressing the conservation of energy between the solar energy absorbed by the Earth system and the energy emitted by the Earth into space:

$$S(1-\alpha) = \sigma T_e^4$$

This relation provides a value of the Earth's temperature in the absence of greenhouse effect:

$$T_e = \left[\frac{S(1-\alpha)}{\sigma}\right]^{1/4} = \left[\frac{238}{5.67\times10^{-8}}\right]^{1/4} = 255\,\mathrm{K} \text{ or } -18\,^{\circ}\mathrm{C}$$

To account for the effect of greenhouse gases, we add an atmospheric layer of absorbing gases to the present model. We assume that this layer is totally opaque to the radiation emitted by the surface, whose temperature is denoted by T_s. With its atmospheric temperature T_a, this atmospheric layer re-emits energy according to Stefan Boltzmann's law, with 50% towards space and 50% towards the ground. We write the energy balance at the top of the atmosphere:

$$S(1-\alpha) = \sigma T_a^{\,4}$$

and the Earth's surface:

$$S(1-\alpha) + \sigma T_a^{\,4} = \sigma T_s^{\,4}$$

By combining these two equations and considering the definition of the effective black body temperature T_e, we can deduce the surface temperature:

$$T_s = 2^{1/4}\ T_e = 1.19\ \ T_e = 303\,\mathrm{K} = 30\,^{\circ}\mathrm{C}$$

and atmospheric temperature:

$$T_a = T_e = 255\,\mathrm{K} = -18\,^{\circ}\mathrm{C}$$

This shows that the presence of an absorbing layer in the atmosphere leads to a very significant increase in surface temperature. With the assumptions adopted, we obtain an average temperature of 30 °C. A more detailed and comprehensive model, which yields more realistic average temperatures (15 °C), takes into account other elements: first, the atmosphere is not completely opaque to terrestrial radiation; second, greenhouse gases are distributed throughout the atmosphere with a temperature that varies with altitude; and third, part of the solar radiation is absorbed and scattered by the molecules and particles present in the atmosphere. A more detailed formulation also takes into account the geographical distribution of the incoming solar energy. In 1969, the two pioneers of climate modeling, the American meteorologist William D. Sellers (1928-2014), professor at the University of Arizona, and the Soviet climatologist Mikhail Ivanovich Budyko (1920-2001), member of the Russian Institute of Hydrology, expressed the conservation of energy in the Earth system as follows

$$S(\phi)[1-\alpha(\phi)] = [A + BT_s(\phi)] + K\left[T_s(\phi) - \overline{T_s}\right]$$

In this expression $S(\phi)$ is the mean incident solar energy at latitude ϕ and $\alpha(\phi)$ is the albedo, which varies with the type of soil, considering in particular the presence of snow and ice at high latitudes. The first term in the right-hand side of the equation expresses the loss of terrestrial energy to

space, using a linearized form of the Stefan-Boltzmann law with constants A = 204 W m^{-2} and B = 2.17 W m^{-2} K^{-1}. The second term on this right-hand side represents the net heat transport with latitude; in this simple linearized formulation, the intensity of heat transport is assumed to be proportional to the difference between the surface temperature $T_s(\phi)$ at latitude ϕ and the global mean surface temperature $\overline{T_s}$ with a transport coefficient K of the order of 3.80 W m^{-2} K^{-1}.

8
The Photochemical Reactor

Since the seventeenth century, successive generations of chemists have developed ingenious experimental methods to study the nature of the fluid that surrounds the earth. They were able to determine that air is a mixture of different chemical elements, rather than a simple, indivisible body as the scholars of antiquity and the Middle Ages thought. In a book published in 1864 entitled *Physical Geography for Schools and the General Readers*, Commander Matthew Fontaine Maury (1806-1873) of the U.S. Navy emphasized the Earth system's ability to remove man-made air pollutants from the atmosphere:

> "Chemists tell us, and observation teaches, that with every breath we draw and every fire we light the atmosphere is corrupted. Everything that has breath so corrupts the air which is taken into the lungs that when it is cast forth it is no longer fit for wholesome respiration. Now, if in the physical economy some arrangement had not been provided by which the atmosphere could get rid of these impurities, the whole air would, in the process of bygone ages, have ere this become so tainted as to be no longer suitable for respiration, and man would perish from the earth through lack of wholesome air."

At that time, the destruction of atmospheric pollutants was attributed to the presence of vegetation rather than to chemical processes in the air that had not yet been identified.

What was known about the chemical composition of air at the end of the 19th century? The work of Henry Cavendish in 1781, followed by the investigation of Joseph Louis Gay-Lussac and Alexander von Humboldt in 1805, as well as the studies of Jean-Baptiste Dumas (1800-1884) and Jean-Baptiste Boussingault (1800-1887) in 1841, showed that air is essentially composed of nitrogen (N_2) and oxygen (O_2) in proportions that vary little with geographic region or altitude. These proportions are approximately 78% and 21%, respectively. In addition to these stable and dominant gases, there are the noble gases identified by Lord Rayleigh and Sir William Ramsay (argon with a volume content of 1/100 and, in lower concentrations, helium, krypton, neon and xenon), as well as other trace gases: These include water vapor (H_2O), which is composed of one oxygen atom and two hydrogen atoms and whose atmospheric content varies considerably with time and place (typically from 1/1000 to 1/30 by volume), and carbon dioxide (CO_2), whose content at that time was about 1/3000 by volume.

Since the work of Christian Schönbein, we also know that the air contains what Albert Lévy called "an oxidizing principle more energetic than oxygen", due to the presence of ozone (O_3). For Lévy, this gas was nothing more than "oxygen with exalted properties", and its content, measured at the Parc Montsouris Observatory in Paris, was only 1/108 by volume.

By the early 1900s, we also knew that ammonia, produced largely by the decomposition of organic matter and by the presence of manure, as well as sulfur dioxide (SO_2), and hydrogen sulfide (H_2S), were present in the air. Nitric acid (HNO_3) and nitrous acid (HNO_2) were also known to exist and were thought to be produced by electrical discharges during thunderstorms. Chemists of the time also noted the presence, especially in the vicinity of industrial and mining areas, of hydrocarbons whose chemical nature was not well understood. These compounds existed in addition to the "swamp gas", i.e., methane (CH_4), identified by Alessandro Volta in 1776. Finally, chemists believed that the atmosphere also contains hydrogen (H_2), which is present in small amounts near the ground, while its abundance increases with altitude. In his book on the problems of the atmosphere, published in 1914, Alphonse Berget[281] summarized the state of knowledge on this very point (which changed radically in later years):

> "According to the new views of physicists, it is [...] at an altitude of 75 to 80 kilometers that the region of discontinuity in the constitution of the atmosphere begins.[282] At this height, the total pressure of the air is less than a quarter of a millimeter and 50% of this air consists of hydrogen. At 90 km, one should have [...] 70% hydrogen and at 100 km, 99.5% hydrogen, 0.4% helium and 0.1% nitrogen: oxygen must be completely absent at this altitude."

At the beginning of the twentieth century, atmospheric scientists were asking themselves: is the list of gases identified in the air exhausted, or will it be enriched by the discovery of yet unknown elements or molecules that have not yet been detected? As we will see in the following pages, many chemical species, often in very small quantities, have been observed in the Earth's atmosphere over the course of the twentieth century. The presence of some of these species results from the action of solar photons, whose energy can be sufficient to break the bond between atoms in certain molecules, forming so-called secondary species, which are generally highly reactive. Until the late 1960s, these *photodissociation* processes, also known as *photolysis*, were thought to occur only in the higher layers of the atmosphere, which are capable of absorbing radiation of sufficient energy to break down the molecules. Scientists at the time believed that the lower layers of the atmosphere were protected from high-energy radiation and therefore not subject to photolysis; these layers near the Earth's surface would therefore be chemically quasi-inert, and pollutants would accumulate there without being able to be chemically destroyed. We will see later that this

[281] Berget, A., *Les problèmes de l'atmosphère*, E. Flammarion, Paris, 343 pp., 1914.

[282] At the beginning of the twentieth century, the idea of a transition between two distinct atmospheric regions (today called the homosphere below 90 km and the heterosphere above this altitude) was already being mooted.

view had to be fundamentally revised and that, in reality, the entire atmosphere must be seen as a *photochemical reactor* in which chains of reactions take place to oxidize the species emitted at the Earth's surface. In this chapter, we'll show how far we've come in understanding the foundations of a discipline that has evolved into what we now call *atmospheric chemistry*.

Photochemistry of Stratospheric Ozone

It was probably Sydney Chapman who first introduced the concept of photodissociation in the context of atmospheric problems. At the first Ozone Conference in Paris in 1929, the British physicist suggested that the energy provided by ultraviolet (UV) solar radiation in the stratosphere could break an oxygen molecule into two oxygen atoms. This molecule, which is very stable in the atmosphere, is nevertheless likely to dissociate if the energy of the incident solar photons is sufficiently high (i.e., in this case, if the wavelength of the radiation is less than 242 nm). This process is described by the symbolic equation:

$$\text{(R1)} \qquad O_2 + \text{radiation} \rightarrow O + O$$

Since the rate at which the resulting oxygen atoms recombine decreases with atmospheric pressure, the lifetime of the oxygen atom, which is short in the lower layers of the atmosphere, becomes larger at high altitudes. In proposing this photochemical mechanism, Chapman showed why oxygen in the upper atmosphere is essentially in atomic rather than molecular form. The recombination of atomic oxygen occurs by one of the following mechanisms:

$$\text{(R2)} \qquad O + O \rightarrow O_2$$

or

$$\text{(R3)} \qquad O + O_2 \rightarrow O_3$$

The second process, which dominates in the troposphere and stratosphere, results in the formation of an ozone molecule (O_3). This latter molecule is photodissociated by solar radiation (in this case, ultraviolet and visible radiation):

$$\text{(R4)} \qquad O_3 + \text{radiation} \rightarrow O + O_2$$

Actually, this photochemical reaction does not contribute to the net destruction of atmospheric ozone because the oxygen atom that is produced recombines to reform the ozone molecule. The actual ozone-destroying mechanism occurs when an oxygen atom collides with an ozone molecule, resulting in the reformation of molecular oxygen:

$$\text{(R5)} \qquad O + O_3 \rightarrow O_2 + O_2$$

However, this latter reaction is relatively slow, too slow to explain the observed values of ozone concentration in the atmosphere. The Chapman's mechanism must therefore be supplemented by other mechanisms that accelerate reaction (R5).

It wasn't until 1950 that Sir David Bates and Baron Marcel Nicolet, whose work is mentioned in Chapter 7, introduced additional reactions that could

accelerate ozone destruction by involving the presence of hydrogen species (H, OH). The sequence

$$\text{(R6)} \qquad H + O_3 \rightarrow OH + O_2$$

$$\text{(R7)} \qquad OH + O \rightarrow H + O_2$$

is a so-called *catalytic* cycle because the hydrogen atom H (the catalytic agent) remains unchanged at the end of the process; it can therefore be repeated many times, with each cycle destroying one oxygen atom and one ozone molecule. Other catalytic cycles involving hydrogen compounds contribute to ozone destruction. When all these hydrogen-related mechanisms are considered, the calculated ozone concentrations are consistent with those observed in the mesosphere (above 50 km).

In 1964, John Hampson[283] at the *Établissement de recherches et de perfectionnement de l'armement* in Val Cartier, Quebec, attempted to explain why mathematical models overestimated the amount of ozone in the stratosphere (below 50 km). He claimed that these models lacked an adequate representation of the hydrogen chemistry that could destroy the ozone molecule. However, calculations using reaction kinetic constants measured in the laboratory show that the effect of hydrogen radicals is insufficient to provide the hoped-for explanation below 50 km altitude. It was not until the early 1970s that theoretical calculations based on additional photochemical processes were able to reproduce the measured values of stratospheric ozone concentration.

In the 1970s, forty years after Chapman's work and twenty years after the study of Bates and Nicolet, decisive progress was made in stratospheric ozone chemistry. Paul Jozef Crutzen (1933-2021), who developed a mathematical model of stratospheric chemistry, found that the photochemical process that dominates ozone destruction is a cycle catalyzed by nitric oxide (NO):

$$\text{(R8)} \qquad NO + O_3 \rightarrow NO_2 + O_2$$

$$\text{(R9)} \qquad NO_2 + O \rightarrow NO + O_2$$

By 1970, the presence of nitric oxide (NO) had not been observed, so Crutzen's conclusion remained speculative. Only one other nitrogen compound, nitric acid (HNO_3), had been detected in the stratosphere (1968) by a group at the University of Denver led by David Murcray (1924-2009). The first measurements

[283] After leaving the Canadian government service in November 1969, Hampson became a professor at Laval University in Quebec. It was in this new capacity that, in July 1974, he published a resounding article in *Nature* entitled "Photochemical war on the atmosphere" (Vol 250, pp 189-191), in which he expressed concern about the changes in photochemical regimes that could result from nuclear explosions. He was astonished that international deliberations on nuclear arms control had ignored this danger, which he considered more serious than the impact of supersonic aircraft on the ozone layer (see Chapter 10). In 1977-1978, while affiliated with York University in Toronto and the University of Western Ontario in London, Ontario, he spent four months at Leningrad University and the Main Geophysical Observatory, where he was hosted by the atmospheric physicist Kirill Yakovlevich Kondratyev (1920-2006) and exchanged ideas on these issues with his Soviet colleagues. In the 1980s, he left Canada for the United Kingdom.

of nitrogen oxides were made in New Mexico in 1973 by Canadian researchers Harold Schiff (1923-2003) and Brian Ridley, using a balloon-borne instrument reaching an altitude of 35 km, which confirmed the presence of NO in the stratosphere[284]. Crutzen showed that the main source of NO is the oxidation in the atmosphere of nitrous oxide N_2O, a molecule produced by bacteria in soils. Clearly, while the origin of ozone in the stratosphere is purely photochemical, its destruction is linked to biological activity on the Earth's surface. Other sources of nitrogen oxide, this time produced by human activity, were mentioned: the release of NO by aircraft engines flying in the stratosphere and the dissociation of molecular nitrogen present in the air under the effect of American and Soviet nuclear explosions, relatively frequent during the nuclear test period of the 1960s. These disturbances were believed to have destroyed significant amounts of ozone in the stratosphere. We will return to this issue in Chapter 10.

Paul Crutzen was an outstanding figure in atmospheric science from the 1970s to 2020 and in Earth system science in general. Born in Amsterdam, he grew up during World War II and the immediate postwar years. The family's financial resources were limited, and instead of attending university, the young Crutzen enrolled in a technical school specializing in civil engineering. This enabled him to begin his career at the Amsterdam Bridge Construction Office. However, attracted by research and innovation, Crutzen responded to an advertisement in a local newspaper for a position as a programmer at Stockholm University. He was hired. It wasn't long, however, before the director of the university's Meteorological Institute, Bert Bolin (1925-2007), suggested that Crutzen begin a university curriculum, which culminated in a bachelor's degree in 1968, and with a doctoral thesis on ozone photochemistry. His work was supervised by Bolin and upper atmosphere and aurora specialist Georg Witt (1930-2014).

After this period in Sweden, Crutzen spent some time at the Clarendon Laboratory of Oxford University, where he wrote the paper attributing to nitrogen oxides the main mechanism of catalytic ozone destruction in the stratosphere. A few years later, in 1973, he submitted his thesis to the University of Stockholm for the title of Doctor of Philosophy: "On the photochemistry of ozone in the stratosphere and troposphere and the pollution of the stratosphere by high-flying aircraft".

Crutzen continued his brilliant career by focusing on the problem of tropospheric ozone and then on the effects of forest fires on the chemical composition of the atmosphere, particularly in the tropics. Other topics of interest included the relationship between atmospheric chemistry and climate and, more generally, the impact of human activity on the environment. It was while observing the effects of a forest fire in the Rocky Mountains of Colorado that he had an idea: Wouldn't the planet burn if a nuclear war broke out? And if it did, wouldn't we see a gigantic rupture in the atmosphere and a cooling of the planet in the form

[284] The measurement method is based on the *chemiluminescence* technique*:* atmospheric NO reacts in the instrument with an ozone molecule to form NO_2 and emits light. By measuring the intensity of this light, the concentration of atmospheric NO can be deduced.

of a veritable "nuclear winter"? And a few years later, he continued his reasoning: if the particles produced by such explosions were likely to cool the Earth, couldn't we counteract the warming linked to the increase in atmospheric CO_2 by injecting sulfate particles into the stratosphere? The concept of *climate intervention* was born, although Crutzen believed that actions to artificially modify the climate were a last resort. Finally, at the end of his career, Crutzen saw human activity as an undertaking of such magnitude that it was determining the evolution of the planet. In other words, for Crutzen, we had changed the geological epoch from the Holocene to a new geological epoch that he called the *Anthropocene*.



FIGURE 8.1: Paul Jozef Crutzen. © Mike Wolff HF/tsp.

After leaving Oxford, Crutzen developed his ideas first in the United States, where in 1977 he became director of the Air Quality Division at the National Center for Atmospheric Research (NCAR) in Boulder, Colorado. In 1980, he was invited to lead the Max Planck Institute for Chemistry in Mainz, Germany, where he succeeded Christian Junge (1912-1996), a prominent specialist in atmospheric aerosols and radioactivity. In 1995, Crutzen was awarded the Nobel Prize in Chemistry for his work on atmospheric ozone.

In a biographical note written in Paul Crutzen's honor, Rolf Müller[285] describes his former teacher as both a brilliant scientist, capable of tackling an impressive range of atmospheric problems, and an engaging, unassuming personality with an excellent sense of humor and a spirit of friendship.

By the mid-1970s, it seemed likely that the stratospheric ozone problem had been solved. However, at a conference in Kyoto, Japan, in September 1973, Richard S. Stolarski (1943-2024) and Ralph John Cicerone (1943-2016), working at the University of Michigan in Ann Arbor, added a mechanism involving the chlorine atom to the photochemical schemes of Bates and Nicolet and Crutzen:

$$\text{(R10)} \qquad Cl + O_3 \rightarrow ClO + O_2$$

$$\text{(R11)} \qquad ClO + O \rightarrow Cl + O_2$$

The sources of chlorine in the atmosphere had not all been identified, but volcanic eruptions and ocean emissions were considered the most important natural sources. A year later, two chemists from the University of California at Irvine, Mario Molina (1943-2020) and F. Sherwood (Sherry) Rowland (1927-2012)

[285] Müller Rolf, Paul Jozef Crutzen, Royal Society, London, 2022.



FIGURE 8.2: Ralf Cicerone (left) and Richard Stolarski (right) Sources: National Academy of Science and AGU.

mentioned a source of industrial origin that had not yet been considered but was most likely the dominant source of stratospheric chlorine since the 1960s. This source was provided by the release into the atmosphere of chlorofluorocarbons, i.e., organic compounds used at the time as propellants in aerosol cans or as refrigerants in air conditioning systems.

Stolarksi continued his career at NASA's Goddard Space Science Center near Washington. As for Cicerone, his career took him to the Scripps Institution of Oceanography in San Diego, California, and then to the National Center for Atmospheric Research in Boulder, Colorado, where he headed the Atmospheric Chemistry Division. He then taught at the University of California at Irvine, where he became provost, and finally joined the U.S. Academy of Sciences, where he served as president.

In 1975, Steven C. Wofsy, Michael B. McElroy, and Yuk I. Yung of Harvard University showed that bromine also contributes to the catalytic destruction of ozone in the stratosphere.

Carbon Monoxide Photochemistry

A few months after Bates and Nicolet had published an article in 1950 highlighting the role of the hydroxyl radical OH, in the destruction of ozone at high altitudes, David Bates and Agnes E. Witherspoon began to investigate the mechanisms that could produce or destroy other chemical species in the atmosphere, particularly carbon monoxide (CO). Several observations were emerging that guided the analyses of these atmospheric chemists.

We have already mentioned the work of the astrophysicist Marcel Migeotte (1912-1992). In 1949, he detected a line in the solar infrared spectrum at a wavelength of 4.7 micrometers, which he attributed to the absorption of solar radiation by carbon monoxide (CO), probably present in the Earth's atmosphere.

Subsequent measurements at the Jungfraujoch station in the Swiss Alps provided a first estimate of the atmospheric CO content: it was estimated to be on the order of 100 ppbv[286].

Atmospheric scientists immediately imagined that the photodissociation of CO_2 could be a significant source of CO, but this photochemical process requires high energy. It can therefore only occur at very high altitudes, i.e., in layers accessible to shortwave ultraviolet radiation. Another source of CO, this time at ground level, is the combustion of coal and other fossil fuels. The role of road traffic had been mentioned, and carbon monoxide therefore, appeared to be a more abundant pollutant near industrial and urban sources than in remote areas.

The degree to which carbon monoxide disperses in the atmosphere and reaches geographic regions distant from primary sources depends on how long the molecule remains in the atmosphere, and therefore on its ability to be destroyed. Bates and Whiterspoon proposed that the destruction of CO results from the reaction of this molecule with the hydroxyl radical OH, which produces CO_2 and converts OH to a hydroperoxyl radical HO_2. Once again, the importance of the OH radical was emphasized. With the knowledge gained in the early 1950s, it became apparent that atmospheric carbon is essentially in the form of dioxide below 90 km and monoxide above 110 km. In addition, early estimates of the lifetime of CO resulting from combustion were inaccurate but estimated to be less than 4 years. We now know that the lifetime of carbon monoxide is on the order of 2 or 3 months.

The Metastable Oxygen Atom

In a remarkable book[287] published in 1961, the American chemist Philip A. Leighton (1897-1983) of Stanford University summarized the state of knowledge of photochemical processes as they were known at the time. He wrote:

> "One of the most striking developments of the past decade, both in the field of air pollution and in that of atmospheric chemistry, has been the recognition that photochemical reactions, produced by sunlight, may convert relatively innocuous pollutants into substances which constitute a nuisance, create a possible health hazard, and cause economic loss to man."

In his book, Leighton pointed out that the oxygen atom produced by the photodissociation of ozone (reaction R4 in Chapman's mechanism - see above) is in the ground state (labeled ^3P by spectroscopists) when the incident solar radiation that dissociates the ozone molecule consists of visible light. However, if this radiation is more energetic and is part of the ultraviolet spectrum, the atom is produced in an excited electronic state (labeled ^1D). This is called a metastable

[286] ppbv = parts per billion by volume.

[287] Leighton, P.A., *Photochemistry of Air Pollution*, Academic Press, New York, 300 pp., 1961.

state[288]. In general, in the lower and middle layers of the atmosphere, the $O(^1D)$ atom is rapidly de-excited by collisions with surrounding molecules, and the excess energy provided by its excited state is converted to thermal energy. The formation and conversion of the $O(^1D)$ atom into an $O(^3P)$ atom takes place in a matter of microseconds in these atmospheric layers, so that the total mass of the metastable $O(^1D)$ atom in the entire atmosphere is at most a few grams. The mass of a paper clip! However, as we will see in the following pages, a small fraction of these atoms, instead of being de-excited back to their ground state, can react with other atmospheric species present in the atmosphere.

It was undoubtedly Richard Dunbar Cadle (1914-2010) who first recognized the importance of the $O(^1D)$ atom in atmospheric chemistry. In a too-often-forgotten article[289] published in 1963, this chemist, who had just joined the National Center for Atmospheric Research (NCAR), wrote:

> "Atomic oxygen, electronically excited to the ^1D state in the atmosphere, is interesting for at least two reasons. The first is that it is responsible for the [...] red lines in the airglow and aurora. The other is the possibility [...] that it competes with ground-state atomic oxygen (^3P) in certain chemical reactions."

He noted that, in the atmosphere, concentrations of $O(^1D)$ are considerably lower than those of $O(^3P)$, but that certain reactions are favored when they occur with excited oxygen $O(^1D)$ rather than with ground-state oxygen $O(^3P)$. Cadle added that the reaction of $O(^1D)$ with water vapor (H_2O) should produce two hydroxyl radicals (OH), a possibility already raised by Leighton in his book, but the rate of this reaction and therefore the importance of this process were not known in the early 1960s.

As we will see later, by emphasizing the role of the $O(^1D)$ atom, Richard Cadle made a fundamental discovery that allowed us to describe what we now call the atmospheric photochemical reactor. After completing his Ph.D. at the University of Washington, this talented chemist



FIGURE 8.3: Richard D. Cadle. Source: NCAR Archives.

[288] Metastable state: excited state of an atom, nucleus or other system that has a longer lifetime than ordinary excited states, but a shorter lifetime than the lowest-energy, often stable state known as the ground state.

[289] Cadle, R.D., Daytime atmospheric $O(^1D)$, *Discussions of the Faraday Society, 37,* 66-72, 1964.

first worked in the private sector before being hired in 1948 by the Naval Weapons Center at China Lake, California, where he probably met Bates and Nicolet, who visited the facility in 1949. In 1950, Cadle joined the Stanford Research Institute in Menlo Park, also in California, and, in 1963, NCAR in Boulder, CO, where he worked on atmospheric chemistry problems until his retirement in 1979.

OH: The Atmospheric Detergent

Bates and Nicolet were credited with recognizing the central role of free radicals in the atmosphere, particularly the OH radical produced by the photodissociation of water vapor in the mesosphere (above 50 km). Cadle's merit lies in his suggestion of a second OH radical formation process due to the oxidation of water vapor by the metastable oxygen atom $O(^1D)$.

The fundamental role of the OH radical in describing photochemical processes in the troposphere was highlighted in 1971 by Hiram (Chip) Levy II. This work, often described as seminal, shows that the atmosphere has the capacity to oxidize and thus destroy a large number of chemical species, including various pollutants emitted at the Earth's surface. In fact, the OH radical has been described as the "detergent of the atmosphere" and even the "scavenger" of chemical species.

Hiram Levy II's personal and professional trajectory is an interesting one. Born in Rochester, New York, he spent much of his childhood in Bettendorf, a blue-collar suburb of Davenport, Iowa, surrounded by large farms. Levy was destined for farming and ranching; he wanted to be a farmer. This period was marked by the Soviet launch of the first artificial satellite, Sputnik, which Americans remember as a moment of humiliation. The country had to get its act together and give science and technological innovation a prominent place again, especially in school curricula. So, the principal of Levy's school hired a young science teacher to get the students excited. This teacher, Dan Schaeffer, who traveled the roads of Iowa on a Harley-Davidson and whose wife baked excellent chocolate chip cookies for the students, was a revelation to Levy. Nevertheless, he remained true to his original calling, enrolling at Iowa State University to study agronomy. However, he soon became disillusioned with the discipline, which he felt was not rigorous enough. Then he remembered the good advice of his science teacher and decided to change direction. A few years later, he graduated with a degree in chemistry and physics and was ready to start a career in industry. But another surprise awaited



FIGURE 8.4: Hiram Levy II.

him. During an interview at the famous Bell Laboratories, the head of human resources suggested that he pursue a Ph.D. instead of an immediate career. After passing the Graduate Record Examination, a prerequisite for admission to such a program, Levy found himself at Harvard University in Cambridge, near Boston, where he wrote a thesis in applied physical chemistry before joining, as a post-doc, the chemistry department at MIT, located at the other end of "Mass Avenue" that runs through the city of Cambridge.

Levy was then hired at the Smithsonian Astrophysical Observatory, where he worked with Alex Dalgarno (1928-2015), the "father" of molecular astrophysics, who was also a colleague of David Bates in Belfast. The young researcher first asked himself what interesting problem he could work on. At first, he was tempted to try to understand the causes of the famous ozone deficit in the stratosphere. But he quickly gave up on tackling a question that several researchers were already trying to solve. He was then intrigued by the content of the article by David Bates and the astrophysicist Agnes E. Witherspoon mentioned above and regretted that this important work had been forgotten. In fact, Bates' colleagues, generally "aeronomers", specialists in the upper atmosphere, had paid little attention to the processes that take place in the lower layers of the atmosphere. As for air pollution specialists, they had little interest in the chemical processes occurring outside urban areas; they were unaware that chemistry could play an important role on a global scale, far from industrial sources of pollution. The field was thus open, and Levy, encouraged by the clarity of Philip Leighton's book on atmospheric photochemistry, set out to identify the mechanisms describing the formation and destruction of the OH hydroxyl radical in the troposphere. He concentrated on the processes characteristic of an atmosphere that he qualified as "normal," i.e., little disturbed by the effects of human activity. Uncertainties about the chemical mechanisms that produce and destroy OH radicals were considerable, resulting in a lack of knowledge about the lifetime of many chemical species in the atmosphere, i.e., the rate at which pollutants are eliminated by chemical reactions. For example, in 1952, Bates and Whiterspoon estimated the atmospheric lifetime of carbon monoxide (CO), which is destroyed by the OH radical, to be several years. In other words, pollutants such as carbon monoxide, especially those emitted by motor vehicles, would accumulate in the atmosphere and cause significant health problems. In 1969, however, Ford Motor Company chemist Bernard Weinstock (1917-1981), a student of Harold Urey (1893-1981), the renowned University of Chicago chemist and winner of the Nobel Prize in Chemistry (1934), suggested that the atmospheric lifetime of carbon monoxide was only two months, based on measurements of the isotope ^{14}CO. These results highlighted the importance of the OH radical in the destruction of primary pollutants emitted at the Earth's surface.

The mechanism proposed by Levy was based on a chain of reactions initiated by the photodissociation of ozone under the influence of solar radiation. As Cadle had shown, if the incident photons are sufficiently energetic, the oxygen atom formed is in the excited electronic state ^1D and can then react with water vapor to form the hydroxyl radical OH. This powerful oxidant is generally very reactive, attacking a wide range of chemical species present in the atmosphere. While it reacts relatively slowly with methane, which has an atmospheric

lifetime of about 10 years, as Weinstock suggested, it attacks carbon monoxide much more rapidly (18 times faster) and, as chemical kinetics work has shown, non-methane hydrocarbons, which often have very short atmospheric lifetimes.

Based on the laboratory data available at the time, Levy identified a photochemical cycle initiated by the reaction between the OH radical and carbon monoxide (CO) on the one hand, and methane (CH_4) on the other. These reactions convert the OH radical into a hydroperoxyl radical HO_2 or a methylperoxy radical CH_3O_2. The latter two then react with nitric oxide (NO) to restore (i.e., recycle) the OH radical and simultaneously form nitrogen dioxide (NO_2). Photodissociation of the latter species by solar radiation restores nitric oxide NO and produces an oxygen atom O, which combines with O_2 to form the ozone molecule (Reaction R3). This photochemical cycle involving different chemical species (CO, CH_4 and NO) emitted by natural or anthropogenic processes can be repeated many times, recycling OH until the hydrogenated radicals are destroyed by other processes and converted into relatively stable compounds such as hydrogen peroxide (H_2O_2) or nitric acid (HNO_3). For the sake of completeness, it should be noted that the initial oxidation mechanisms of certain hydrocarbons can result from their reaction with ozone on the one hand and with the nitrate radical (NO_3) on the other. These mechanisms dominate at night when the OH radical is in short supply.

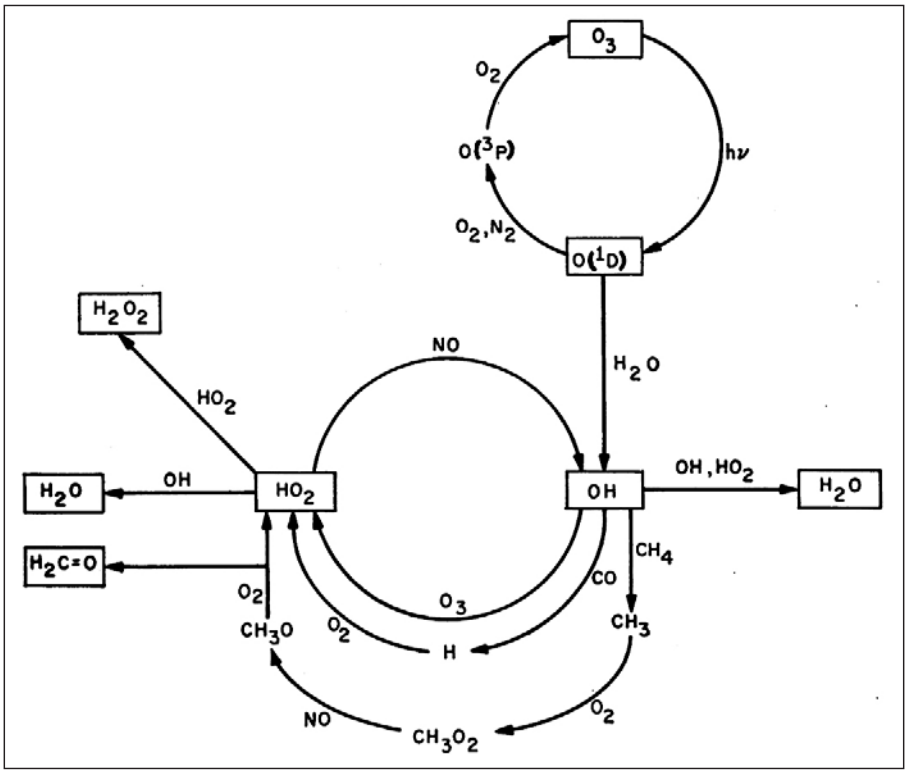


FIGURE 8.5: Photochemical diagram proposed by Hiram Levy in 1971 to explain oxidation processes and, in particular, the role of OH and HO_2radicals in the "normal" atmosphere.

However, it is the OH free radical that largely determines the *oxidizing capacity* of the atmosphere and enables the elimination of most pollutants injected into the air. Paul Crutzen[290] emphasizes the important role of the OH radical:

> "The hydroxyl radical reacts with many gases which otherwise would be inert in the troposphere, such as carbon monoxide (CO), hydrocarbons and chlorinated hydrocarbons. If no OH were present in the troposphere, the atmospheric abundances of these gases would be much larger than observed in the atmosphere, in many cases by orders of magnitude."

Since the 1970s, systematic studies have been carried out to characterize and quantify the emissions of chemical species, either from natural processes (e.g., of biological origin) or from activities related to human activities. The presence of carbon monoxide and nitrogen oxides in the atmosphere is largely the result of anthropogenic processes, in particular the emission of these gases through combustion (automobile and marine traffic, aviation, energy, industry, residential activities, forest fires, biomass burning, etc.). Soil emissions of NO and its production by lightning during thunderstorms, which are particularly frequent in the tropics, are additional sources of nitrogen oxides, but of lesser importance in the mid-latitudes. NO, which is short-lived, is therefore an excellent indicator of human activity, although concentrations of this gas are occasionally high in regions affected by forest fires, sometimes of natural origin. Methane is mainly produced by biological processes in oxygen-deficient ecosystems (swamps, rice fields, etc.). Because of its long lifetime, it is relatively evenly distributed throughout the atmosphere. Most non-methane hydrocarbons, on the other hand, have much shorter lifetimes and are found in significant quantities only near their sources (Box 8.1). Those of anthropogenic origin are therefore most abundant in urban and industrial areas. On the other hand, those of biological origin (e.g., isoprene and terpenes) are mainly found near forests.

Box 8.1. Organic Chemistry in the Atmosphere

The Earth's atmosphere contains thousands of organic compounds. Some of these are highly volatile and therefore exist primarily in a gaseous state. Others condense more readily to form airborne organic particles. The concentration of organic molecules in the atmosphere is generally very low, so these species require sophisticated instrumentation to detect. However, their role is important because they directly influence the oxidizing properties of the atmosphere and contribute to the formation of ozone and organic aerosols. The first laboratory studies of organic molecules were carried out in the nineteenth century.

Hydrocarbons are represented by the general molecular formula C_nH_m. Among those qualified as "primary" (i.e., directly emitted at the Earth's

[290] Crutzen, P.J., The role of NO and NO_2 in the chemistry of the troposphere and stratosphere. *Annual Review of Earth and Planetary Sciences, 7*, 443-472, 1979.

surface), a distinction is made between biogenic and anthropogenic compounds. The most important compounds of biological origin are isoprene (C_5H_8) and terpenes ($C_{10}H_{16}$). The first was identified by the English chemist Charles Greville Williams (1829-1910) while distilling natural rubber. He derived the name "isoprene" from the prefix iso (equal) and a contracted form of the word propylene. Approximately 450 tetragrams of isoprene are released into the atmosphere each year by vegetation, primarily trees such as oaks, poplars, and eucalyptus. Along with methane, isoprene emissions are the largest source of hydrocarbons in the atmosphere. The name "terpene" is attributed to the German chemist Auguste Kekulé von Stradonitz (1829-1896).

In addition to these biogenic compounds, there are substances of anthropogenic origin. These are grouped into different classes (the symbol *R* stands for an organic chain containing one or more carbon atoms and hydrogen atoms):

Alkanes are saturated hydrocarbons with an *R-H* structure, whose formula is generally written C_nH_{2n+2} with $n = 1, 2, 3,...$ They are produced mainly by the extraction of fossil fuels and the evaporation of gasoline. They are also used as raw materials in the chemical industry. This class includes methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), etc.

Alkenes (C_nH_{2n}) are unsaturated hydrocarbons whose *R* chain contains at least one double bond between carbon atoms. They are largely produced by the petroleum industry and by automobile exhausts. They include ethene or ethylene (C_2H_4) and propene or propylene (C_3H_6).

Alkynes (C_nH_{2n-2}) have at least one triple bond between carbon atoms. This class of hydrocarbons includes ethyne (C_2H_2), also known as acetylene.

Aromatics are cyclic molecules that are abundant in automobile exhaust fumes. Some of them are carcinogenic. These include benzene (C_6H_6), toluene (C_7H_8) and xylene (C_8H_{10}).

Hydrocarbons have been the subject of laboratory studies since the mid-nineteenth century. The discovery of ethane (1834) is attributed to Michael Faraday (1791-1867), that of propane (1857) to French chemist Marcelin Berthelot (1827-1907), and that of butane (1849) to British chemist Sir Edward Frankland (1925-1899). Propene was discovered in 1850 by British cavalry officer John Williams Reynolds (1817-1874), acetylene in 1836 by Edmund Davy (1785-1857), then rediscovered in 1860 by Marcelin Berthelot, who named the molecule acetylene. Benzene was isolated and identified in 1825 by Michael Faraday and synthesized in 1833 by the German chemist Eilhard Mitscherlich (1794-1863). In 1865, Kekuké, who had discovered the tetravalence of carbon, showed that benzene has a cyclic structure represented by a ring of six carbon atoms linked alternately by single and double bonds. Toluene was identified by Polish chemist Philippe Walter (1810-1847), then by French chemists Henri Sainte-Claire Deville (1818-1881) and Auguste Cahours (1813-1991). The latter also isolated xylene in 1850. The term *aromatic* was introduced in 1855 by German

chemist August Wilhelm von Hofmann (1818-1892), in reference to the intense odor emitted by these chemicals.

The photo-oxidation of hydrocarbons in the atmosphere leads to the formation of partially oxidized species, notably *carbonyls* [a molecule composed of a carbon atom double-bonded to an oxygen atom C=O] to which *aldehydes* belong, R-CHO [e.g., formaldehyde, CH_2O, and acetaldehyde, CH_3CHO], and *ketones*, *R-CO-* [e.g., acetone, CH_3COCH_3, and butanone, $CH_3COCH_2CH_3$]. These oxidized species also include *alcohols*, *R-OH* [with methanol CH_3OH, and ethanol, CH_3CH_2OH], *carboxylic acids*, *R-CO*(OH) [with formic, HCO(OH) and acetic acids, $CH_3CO(OOH)$], *organic hydroperoxides R-OOH*, [with methyl hydroperoxide, $CH_3(OOH)$], *peroxycarboxylic acids R-CO*(OOH), [with peracetic acid, $CH_3CO(OOH)$], *organic nitrates* R-ONO_2, [with methyl nitrate, $CH_3(ONO_2)$ and ethyl nitrate, $CH_3CH_2(ONO_2)$], R-$OONO_2$ [with peroxymethyl nitrate, $CH_3(OONO_2)$], and *R-CO*($OONO_2$) [with peroxyacetyl nitrate ($CH_3CO(OONO_2)$].

The oxidation chain of hydrocarbons is initiated by a reaction with the hydroxyl radical (OH) during the day, with the nitrate radical (NO_3) at night, or in the case of alkenes, with ozone (O_3). It is the most rapid of these reactions, generally involving the OH radical, that determines the lifetime of hydrocarbons in the atmosphere. This lifetime varies greatly from species to species: it is about ten years for methane and two months for ethane, but only ten days for benzene and two days for toluene. It is a few hours for biogenic compounds such as isoprene and terpenes, and even a few minutes for certain long-chain compounds such as sesquiterpenes. ($C_{15}H_{24}$).

The first product of these oxidation reactions is the *peroxy radical* RO_2 (CH_3O_2 in the case of methane oxidation). This radical reacts with nitric oxide NO, to form the *alkoxy radical* RO. This reaction converts NO to NO_2, a major source of ozone in the troposphere (see Box 8.2). Very quickly, by reaction with an oxygen molecule O_2, the RO radical is converted into an aldehyde molecule R'CHO, for example, formaldehyde (H-CHO) or acetaldehyde (CH_3-HCO).

Formaldehyde, first identified in 1859 by the Russian chemist Aleksandr Butlerov (1828-1886), was formally identified in 1868 by August Wilhelm von Hofmann. It is not only produced by the oxidation of hydrocarbons, but is also emitted by anthropogenic processes, especially in the petrochemical industry. It persists in the atmosphere from a few hours to a few days, depending on environmental conditions. It is considered a carcinogen.

Acetaldehyde was first observed by Carl Wilhelm Scheele in 1774 but was the subject of numerous studies in the early nineteenth century, notably by Antoine-François comte de Fourcroy (1755-1809), Louis Nicolas Vauquelin (1763-1829), John Wolfgang Döbereiner (1780-1849) and Justus von Liebig (1803-1873). Its main source in the atmosphere is the oxidation of alkanes, alkenes, and ethanol. Other important sources are direct emissions from the ocean and continental biosphere. The lifetime of acetaldehyde in the atmosphere ranges from a few hours to a day or two, depending on photochemical conditions.

The oxidation reactions of R'CHO aldehydes by OH and NO_3 radicals and by ozone *ultimately* lead to the formation of CO_2 and H_2O, thus concluding the hydrocarbon oxidation process.

By reacting with NO or NO_2, the radical RO_2 can also produce organic nitrates of the type R-ONO_2 and $ROONO_2$. Very often, $ROONO_2$ is thermally unstable, so that this compound decomposes rapidly and is therefore very scarce in the air. This is not the case, however, with *peroxyacetyl nitrate* ($CH_3C(O)OONO_2$), which is stable at relatively low temperatures. It is therefore often abundant in the air, especially in polluted regions during winter, and can transport appreciable quantities of reactive nitrogen over long distances.

In NO-poor environments, instead of forming nitrates, RO_2 reacts with the HO_2 radical to form an *organic peroxide* molecule *R*-OOH, a soluble species that can therefore be partially removed from the atmosphere by precipitation. The reaction combining two organic *peroxy* radicals of type RO_2 can lead to the formation of an alcohol *R*-OH, e.g., methanol (CH_3-OH) or ethanol (C_2H_5-OH), and an aldehyde *R*-CHO, e.g., formaldehyde.

Methanol, sometimes called *wood spirit*, was already known to the ancient Egyptians; it was isolated in 1661 by Robert Boyle, and its elemental composition was established in 1834 by French chemists Jean-Baptiste Dumas (1800-1884) and Eugène Péligot (1811-1890). This gas is the most abundant organic constituent in the atmosphere after methane. Its main source in the air comes from emissions by terrestrial vegetation, and its lifetime in the atmosphere is around five days.

Ethanol (C_2H_5-OH), produced in prehistoric times by the fermentation of sugars, was produced in the laboratory in 1769 by the German chemist Johann Tobias Lowitz (1757-1804); its chemical formula was determined in 1808 by Nicolas Théodore de Saussure (1767-1845). The main origin of this gas is biological, e.g., continental vegetation, but industrial activity and biofuels also contribute to the atmospheric abundance. The lifetime of ethanol in the atmosphere is around three days.

Several organic species can now be detected from space. These include methane (CH_4), formaldehyde (H-CHO), methanol (CH_3OH), formic acid (HCO(OH)) and glyoxal (CHOCHO). The latter molecule was first synthesized in 1856 by the German chemist Heinrich Debus (1824-1915). As a significant proportion of formaldehyde and glyoxal is derived from the oxidation of isoprene, measurements of the atmospheric content of the latter two species provide information on the isoprene budget.

Ozone in the Troposphere

Since the work of Arie Haagen-Smit in the 1940s (see Chapter 1), we know that ozone episodes occur during the summer months in urban areas such as Los Angeles or Mexico City. But is tropospheric ozone limited to urban and industrial areas? Or is the pollution by tropospheric ozone a global issue? If so, how is tropospheric ozone produced, destroyed, and transported in the atmosphere?

The first explanation was proposed in 1941 by Erich Regener. The German scientist proposed that tropospheric ozone, which accounts for only 10% of total ozone, originates mainly in the stratosphere, where it is formed from the photodissociation of molecular oxygen by ultraviolet solar radiation. This hypothesis was taken up by the chemist Christian Junge in 1962 and by two other atmospheric scientists in the 1970s: Edwin F. Danielsen (1917-1994), first at the University of Washington in Seattle and then at the National Center for Atmospheric Research in Boulder, Colorado, and Volker Mohnen (1937-2022) at the State University of New York at Albany. According to these two scientists, ozone is injected by air intrusions that occur sporadically when the tropopause deforms[291]. As for the destruction of this gas, it would result from the deposition of these molecules on the Earth's surface and, in particular, on the leaves of the continental vegetation.

However, in 1971, two North Carolina researchers, Lyman A. Ripperton III (1944-2000) and Fred M. Vukovich[292] suggested that ozone might be chemically destroyed in the lower layers of the atmosphere:

> "Although reaction with the earth's surface has been considered the major, if not the only, sink for tropospheric ozone, both theoretical considerations and field observation suggest that gas phase reactions are also a major sink."

As a result, the gases present in the troposphere would be less inert than previously thought. Ozone would therefore be exposed to chemical destruction in the air before it is "deposited" and destroyed at the Earth's surface. But, in addition, can ozone be produced by photochemical reactions in the troposphere outside of polluted areas?

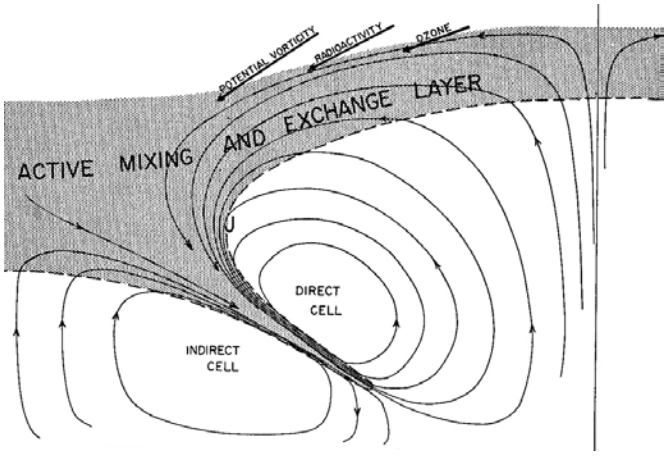


FIGURE 8.6: Schematic representation of the mean circulation in the atmosphere by Edwin Danielsen (then at the University of Hawaii) and of an intrusion of stratospheric air into the troposphere linked to a deformation of the tropopause. Source: Danielsen, E.F., *J. Atmos. Sci.,* 25, 502-518, 1968.

[291] This is known as "tropopause folding".

[292] Ripperton, L.A., Vukovich, F.M., Gas phase destruction of tropospheric ozone. *Journal of Geophysical Research, 76*(30), 7328-7333, 1971.

To answer this question, and to try to identify the mechanisms that could lead to the formation of ozone in the troposphere, we must turn again to the work of Arie Haagen-Smit, which focused on the urban - and therefore highly polluted - region of Los Angeles. The Dutch researcher, who worked at the California Institute of Technology, believed that the formation of ozone results from the oxidation by the oxygen atom (O) of organic substances emitted into the atmosphere, mainly by car traffic and industry. The oxygen atom would be produced by the photolysis of nitrogen dioxide (NO_2) under the influence of solar radiation.

The idea that ground-level ozone was also produced photochemically outside urban areas began to gain ground in the 1960s. Researchers such as Heinz-Karl Paetzold[293] (1916-2002) and F. N. Frankiel[294] in Germany and W. S. Hering and I. R. Borden[295] in the United States claimed that not all tropospheric ozone could originate in the stratosphere. In 1971, Lyman A. Ripperton[296] and his colleagues at the University of North Carolina wrote:

> "Observational and experimental data suggest or demonstrate that some of the nonurban, tropospheric ozone is synthesized in situ rather than being transported from the stratosphere."

However, the Haagen-Smit mechanism did not adequately explain the production of ozone. In the early 1970s, Kenneth L. Demerjian and his colleagues at the State University of New York at Albany proposed to replace this mechanism with a reaction scheme in which the oxidation of organic substances is due to the action of the hydroxyl radical (OH) rather than that of the oxygen atom (O). This scheme can be applied outside urban areas to explain ozone formation. Away from the most reactive sources of volatile organic compounds (VOCs), the oxidation of methane and carbon monoxide in the presence of nitrogen oxides (NO and NO_2) leads to the formation of the ozone molecule. It remained to be determined whether nitrogen oxide was present outside urban and industrial areas. The first attempts, made in 1957 and 1958 by James P. Lodge[297] (1926-2001) and his colleagues at the *Taft Sanitary Engineering Center* in Cincinnati, Ohio, to measure NO_2 levels in the atmosphere over the Pacific Ocean between San Francisco and Hawaii, were unsuccessful; the presence of nitrogen oxides was

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[293] Paetzold, K., "Chemical Reactions in the Lower and Upper Atmosphere," *Interscience*, New York, p 181, 1961.

[294] Frenkiel, F.N., *International Union of Geodesy and Geophysics*, Monographs 1-7, Monograph 3, p. 35, 1960.

[295] Hering, W.S., Borden, I.R., Jr, "*Ozonesonde Observations over North America*," Volume 4, Clearinghouse, Department of Commerce, Washington, D.C., 1967.

[296] Ripperton, L.A., Jeffries, H., Worth, J.J.B., Natural synthesis of ozone in the troposphere. *Environmental Science & Technology, 5*(3), 246-248, 1971.

[297] An alumnus of the Universities of Illinois (Urbana) and Rochester, NY, James P. Lodge, Jr. worked from 1952 in the Meteorology Department of the University of Chicago before joining the Air Pollution Division of the U.S. Public Health Service at the Robert A. Taft Sanitary Engineering Center in 1956. In 1961, he was hired at the National Center for Atmospheric Research in Boulder, CO, where he set up a program on air pollution and, more specifically, on the chemistry of precipitation.

not detected by the instrumentation aboard the meteorological vessels deployed in this region. Nearly twenty years later, in 1976, Richard Anthony (Tony) Cox reported that NO concentrations were below 200 ppt[298] and NO_2 below 400 ppt in (unpolluted) marine air masses along the Irish coast. However, it wasn't until the measurements were made in 1978 by a team from NOAA's Aeronomy Laboratory in Boulder, Colorado, that the first very precise quantitative values were obtained. The campaign organized in the equatorial regions of the Pacific under the direction of Mack McFarland (1947-2022) aboard the oceanographic vessel *RV Knorr* showed that, in oceanic regions, air contains only a few molecules of NO for every 1 trillion molecules of air (average concentration 4 ppt). In the late 1980s, Douglas D. Davis (1940-2016), a chemical kinetics specialist at the Georgia Institute of Technology, measured concentrations of nitrogen oxide over the Pacific Ocean that were 100 times lower than those observed in urban areas, but still sufficient to contribute to ozone formation in regions far from major cities. Similar values were measured by Brian Ridley at the Mauna Loa station (Hawaii) in the early 1990s.

In 1973, a complete photochemical theory of ozone formation was developed by Yale University graduate student William (Bill) Chameides and his professor James Walker (1939-2022). A similar theory was provided by Paul Crutzen, who was then working in the United Kingdom (Box 8.2).

Bill Chameides is an extraordinary person. Born in New York City, where his father ran a neighborhood movie theater, he was destined for a career as a lawyer and began studying law. But he soon changed direction and enrolled in physics courses at New York University in Binghamton before turning to atmospheric science. He did his postdoctoral work at the University of Michigan, working with Ralph Cicerone. He was quickly recognized as a talented scientist and was hired as a professor and researcher by several prestigious universities: the Georgia Institute of Technology (Georgia Tech) and Duke University in North Carolina. In 1998, he was elected to the U.S. Academy of Sciences, and in 2005, he became the scientific director of the non-governmental *Environmental Defense Fund* (EDF). His goal was to elucidate the causes of environmental change at global, regional, and urban scales and to find sustainable solutions for the planet. He was particularly interested in photochemical processes in the lower layers of the atmosphere and, in particular, the impact of environmental change on global food production. He was also a brilliant spokesman for the scientific community on climate change issues.

One day, however, he considered his mission accomplished and announced that his career was changing direction:

> "When I was young, I had two dreams: to become an actor and to become a scientist specializing in environmental issues. I chose the second option first. I had a rewarding career and learned so much. But I woke up one morning and realized that my work as a scientist had come to an end and that it was time to pursue my other dream, that of becoming an actor. And this was to the surprise and, in many cases, dismay of my scientific colleagues."

[298] 1 ppt corresponds to 1 molecule per 10^{12} or per 1000 billion air molecules.

He then turned to acting, appearing on the New York stage in several plays, including *Copenhagen* (the story of Werner Heisenberg's visit to Niels Bohr during the Second World War). He also appeared in several successful films, including *Sugar Creek Gang* (2005).



FIGURE 8.7: William (Bill) Chameides. © DR.

While preparing his Ph.D. at Yale, Chameides noted that *Chip Levy* had shown that the methane oxidation chain is an important source of tropospheric ozone on a global scale, including in regions far from urban and industrial areas. This source appears to exceed that resulting from the injection of stratospheric air into the troposphere. Chameides wrote:

> "We have therefore constructed a photochemical model for tropospheric ozone. We argue that the seasonal and daily variations in the ozone density in the troposphere are for the most part caused by changes in photochemistry rather than by changes in the rate of transfer of ozone-rich stratospheric air into the troposphere. Of course, in some instances, particularly when pronounced peaks in the tropospheric ozone are observed near the tropopause, a strong transfer of stratospheric air is indicated. As long as this packet of air remains intact, low concentrations of odd nitrogen oxides and water vapor thus being maintained, it will exhibit an ozone density characteristic of the stratosphere. Nevertheless, it is our belief that, on the average, photochemical processes typical of the troposphere determine the tropospheric abundance of ozone."

Subsequent studies of photochemical mechanisms applied to the troposphere, notably by Paul Crutzen and his team, confirmed Chameides' conclusions: ground-level ozone formation does indeed result from the photo-oxidation of carbon monoxide, methane, and other hydrocarbons in the presence of nitrogen oxides. However, these studies also demonstrate the non-linear nature of the processes involved and the existence of different photochemical regimes. In regions with little or no pollution, such as rural continental areas, ozone production is limited by the amount of nitrogen oxides available. On the other hand, in extremely polluted regions rich in nitrogen oxides, such as the centers of large metropolitan areas, ozone production is limited by the availability of hydrocarbons. In this case, instead of producing ozone, nitrogen oxides reduce their concentration by chemical titration[299]. The existence of different photochemical environments in the atmosphere therefore, requires appropriate strategies to reduce ozone pollution.

[299] That is, by the reaction $O_3 + NO \rightarrow NO_2 + O_2$. Under the effect of this reaction, ozone is largely converted into nitrogen dioxide. Conversion is almost complete at night, but only partial during the day, as the photodissociation of NO_2 leads to the reformation of ozone molecules.

Box 8.2. Tropospheric Ozone Photochemistry

Oxidation processes in the atmosphere and the resulting formation of ozone are governed by a three-step reaction chain:

First Step: Initiation of the reaction chain producing free radicals. The photochemical mechanism begins with the photodissociation of ozone by solar radiation with wavelengths below 320 nanometers*:*

(T1) O_3 + radiation (< 320 nm) $\rightarrow O(^1D) + O_2$

The oxygen atom that is produced is in its excited electronic state ^1D; it is usually deactivated to the ground state ^3P by a collision with an atmospheric molecule. However, if this collision occurs with a water vapor molecule, two hydroxyl radicals (OH) are formed:

(T2) $H_2O + O(^1D) \rightarrow OH + OH$

Other mechanisms leading to the formation of OH and HO_2 free radicals have also been identified, including the photolysis of oxygenated organic compounds such as formaldehyde (HCHO).

(T3) HCHO + radiation $\rightarrow 2\ HO_2$

or reactions between certain types of hydrocarbons (alkenes) and ozone.

Second Step: Chain propagation and amplification cycles. The oxidation of carbon monoxide (CO) and hydrocarbons (which we express by the general symbol RH where R represents an organic chain such as CH_3 in the case of methane, C_2H_5 in the case of ethane) by the OH radical leads to the formation of hydroperoxyl radicals (HO_2) and organic peroxy RO_2:

(T4) $CO + OH + O_2 \rightarrow HO_2 + CO_2$

(T5)[300] $RH + OH + O_2 \rightarrow RO_2 + H_2O$

These peroxyl radicals react with nitric oxide

(T6) $HO_2 + NO \rightarrow NO_2 + OH$

(T7) $RO_2 + NO \rightarrow NO_2 + RO$

to form nitrogen dioxide NO_2. Reaction T6 restores the OH radical. As for the alkoxy radical RO which is produced by reaction (T7), it can decompose thermally, but reacts mainly with O_2 to form, for example, a carbonyl (such as formaldehyde HCHO - see reaction T8 - or acetaldehyde) and an HO_2 radical.

(T8) $RO + O_2 \rightarrow R'CHO + HO_2$

The following steps are complex. The photodissociation or oxidation of carbonyls leads to the formation of additional free radicals and may constitute an additional source of ozone through the conversion of NO to NO_2.

[300] Note that Levy introduced this reaction only in the case where the hydrocarbon RH is methane CH_4 and the methyl peroxyl $RO_2 = CH_3O_2$.

Reactions initiated by the oxidation of non-methane hydrocarbons *ultimately* lead to the formation of carbon dioxide and water molecules.

In some cases, organic radicals can react with nitrogen dioxide molecules to form organic nitrates. For example, the acetyl radical (CH_3CO) produced by the oxidation of certain hydrocarbons or resulting directly from combustion, for example, in diesel engines, can react with a molecule of oxygen and a molecule of NO_2 to form peroxyacetyl nitrate ($C_2H_3NO_5$ or PAN). This gas, which is lachrymatory and relatively stable at low temperatures, can carry nitrogen dioxide over long distances, which it releases back into the atmosphere when it thermally decomposes in relatively high-temperature regions. The number of hydrogen radicals produced by the oxidation of a hydrocarbon depends on the quantity of nitrogen oxides present in the atmosphere of the region in question.

The ozone formation mentioned above occurs during the day, due to the photodissociation of NO_2 by solar radiation.

(T9) $NO_2 + \text{radiation} \rightarrow NO + O$

The recombination of the oxygen atom resulting from this reaction leads to the formation of an ozone molecule:

(T10) $O + O_2 \rightarrow O_3$.

To these photochemical processes must be added the intrusion into the troposphere of ozone from the stratosphere (which constitutes an additional source of tropospheric ozone) and the deposition of ozone on the Earth's surface (which constitutes an ozone sink).

As the so-called "primary" pollutants, i.e. those emitted directly into the atmosphere, are essentially the result of human activity, ground-level ozone formed *in situ* is a so-called "secondary" pollutant; it is an important ingredient in the photochemical "smog" frequently observed in urban areas such as Los Angeles or Mexico City. Its concentration is sensitive to the intensity of solar radiation, peaking in the early afternoon.

As Levy has already pointed out, other reactions convert OH into HO_2 and HO_2 into OH:

(T10) $OH + O_3 \rightarrow HO_2 + O_2$

(T11) $HO_2 + O_3 \rightarrow OH + 2\ O_2$

These reactions are mechanisms for destroying the ozone molecule, in addition to the mechanism for destroying this molecule resulting from reactions T1 and T2.

Third step: closing the reaction chain by destroying the hydroxyl and peroxyl radicals. Two types of mechanisms need to be considered:

When *NOx levels are low,* as is the case in oceanic regions and sparsely populated areas, the most effective reactions for destroying OH, HO_2, and RO_2 radicals are recombination processes between hydrogenated or organic radicals:

(T12) $HO_2 + HO_2 \rightarrow HOOH + O_2$

which produces hydrogen peroxide (HOOH or H_2O_2) and

(T13) $RO_2 + HO_2 \rightarrow ROOH + O_2$

which produces an organic peroxide, ROOH. Since peroxides are soluble in cloud water droplets, they are rapidly eliminated from the atmosphere during precipitation events.

Finally, consider the reaction between OH and HO_2, which produces water vapor:

(T14) $OH + HO_2 \rightarrow H_2O + O_2$

In the case considered here, which corresponds to low NOx levels, the destruction of free radicals results mainly from their recombination, and ozone production is limited by the quantity of nitrogen oxides available in the atmosphere. In other words, when this "nitrogen oxide-limited" photochemical regime applies, the reduction in ozone levels is achieved by reducing NOx emissions.

When *NOx levels are high,* as is the case in polluted areas and particularly in urban and industrial regions, the main OH radical destruction mechanism results from the reaction with NO_2:

(T15) $OH + NO_2 \rightarrow HNO_3$

The nitric acid formed is also water soluble and is therefore largely eliminated from the atmosphere by precipitation. Other processes involved in the elimination of peroxyl radicals by nitrogen oxides must be considered, especially the formation of organic nitrates by reactions of the type:

(T16) $RO_2 + NO \rightarrow$ organic nitrates

When the atmospheric NOx content is high and hydrogen radicals are destroyed by reaction with nitrogen oxides, ozone production is no longer limited by the presence of nitrogen oxides in the atmosphere, but by that of hydrocarbons. In this photochemical regime, described as "saturated with NOx and limited by the availability of volatile organic compounds", reducing the concentration of ozone in the troposphere therefore requires a reduction in hydrocarbon emissions.

In 1970, the U.S. Congress passed the *Clean Air Act* with the goal of improving air quality and, in particular, reducing ground-level ozone pollution (see Box 8.3). Early theoretical studies showed that ozone formation in the United States was generally limited by the amount of hydrocarbons present in the air. Early efforts by environmental regulators, therefore, focused on reducing hydrocarbon and carbon monoxide emissions from automobiles and industry. However, these measures were not successful, although significant results were achieved in the heart of several metropolitan areas. Especially in rural areas, and

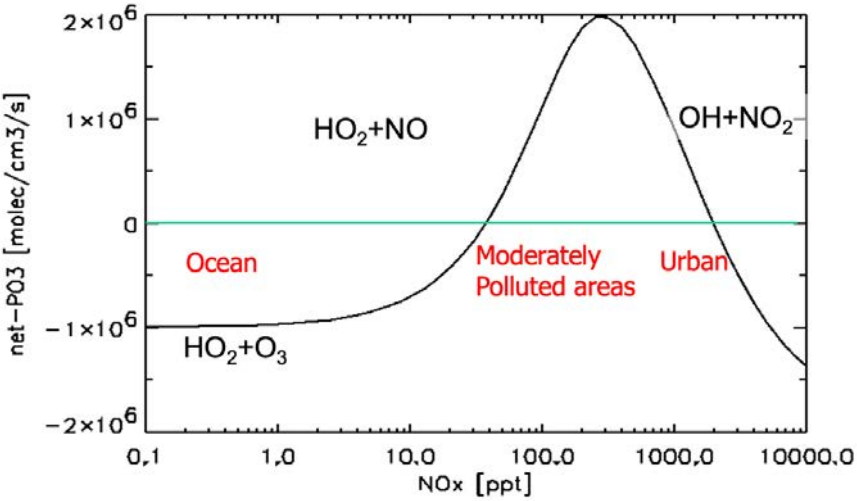


FIGURE 8.8: Net photochemical ozone production as a function of nitrogen oxide (NOx) content. When atmospheric NOx concentrations are very low, ozone is destroyed in particular by the hydroperoxyl radical HO_2. For higher NOx values in moderately polluted areas, photochemical ozone production increases with NOx content. Finally, in highly polluted urban areas, ozone production decreases with NOx content. It is assumed here that concentrations of other species such as hydrocarbons and water vapor remain unchanged.

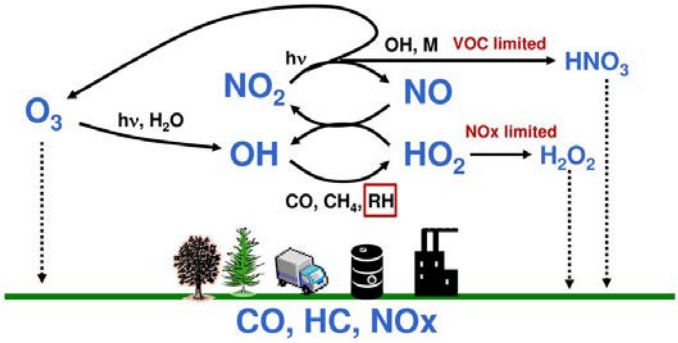


FIGURE 8.9: Schematic representation of the processes leading to ozone formation in the troposphere. The OH radical, produced from ozone and water vapor under the effect of solar radiation, is converted to HO_2 by carbon monoxide (CO), methane (CH_4) and other hydrocarbons (noted RH or HC). The reaction of NO with HO_2 leads to the formation of NO_2, which during the day is photodissociated; the oxygen atom thus formed combines with O_2 to produce ozone. The reaction between NO and HO_2 also reproduces the OH radical, which takes part in a new cycle that generates ozone. In regions where ozone formation is limited by the availability of nitrogen oxides, the destruction of hydrogen radicals is due to the conversion of HO_2 to hydrogen peroxide (H_2O_2). In atmospheres rich in nitrogen oxides, where the conversion of OH to HO_2 and therefore ozone production is limited by the availability of CO, CH_4 and RH, the destruction of hydrogenated radicals is due to the reaction of OH with NO_2 to form nitric acid (HNO_3). Source: Daniel Jacob, Harvard University.

contrary to expectations, ozone levels remained high. The reason for this failure is now understood: the original studies significantly underestimated anthropogenic hydrocarbon emissions and completely ignored the contribution of biogenic (naturally occurring) hydrocarbons. What was not known at the time was that most of the hydrocarbons released into the atmosphere are emitted by vegetation, mainly in the form of two specific compounds: isoprene and terpenes. Taking these additional emissions into account led scientists to a new conclusion: most regions are characterized by a regime in which ozone formation is limited by nitrogen oxides and not, as previously thought, by hydrocarbons. The strategy for controlling ozone pollution had to be radically rethought, and nitrogen oxide emissions had to be tackled.

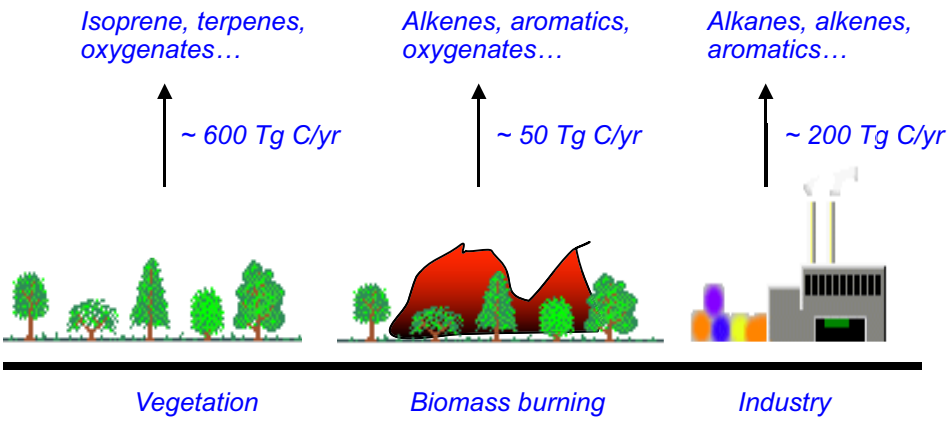


FIGURE 8.10: Hydrocarbon emissions from vegetation, biomass combustion and industrial activities. For each category, the main organic compounds emitted are indicated. The values given refer to the global scale. Note that the main contribution comes from vegetation emissions.

Box 8.3. Pollution from Automobiles

The installation of catalytic converters in motor vehicles has made it possible to significantly reduce exhaust emissions and thus limit the formation of ozone in urban areas. These devices, which are installed in car exhaust pipes, convert the main pollutants into less dangerous products: hydrocarbons and carbon monoxide are oxidized to carbon dioxide (CO_2) and water (H_2O), while nitrogen oxides (NO and NO_2) are reduced to pure nitrogen (N_2). However, these measures have proven to be insufficient to achieve the desired goals, particularly to sufficiently reduce nitrogen oxide concentrations. There are two reasons for this. First, catalytic converters are not very effective when combustion engines are cold, i.e., in the first 10 to 15 km of driving. The same is true when vehicles are traveling at low speeds, such as in traffic jams. On the other hand, the two-way catalytic converters fitted

to diesel cars do not eliminate nitrogen oxide emissions. In the absence of suitable filters, diesel engines also emit carbon particles. Finally, there is a difference between the emissions measured when pollutants are tested in the laboratory (or at a test station) and when they are tested on the road under normal vehicle operating conditions. It should also be noted that in recent decades, new types of pollutants have been emitted into the atmosphere and transported over long distances, such as heavy metals like platinum, rhodium, and palladium, as evidenced by the increasing amounts of these metals trapped in the ice of Greenland and Antarctica. Microplastic particles originating from the tires and brakes of the vehicles are also released into the atmosphere.

Observations of Tropospheric Chemical Species on a Global Scale

The first studies of tropospheric photochemistry in the 1970s were essentially based on simplified mathematical models that reflected the state of knowledge at the time. The goal was to compare the results of these models with values directly observed in the atmosphere. The challenge was enormous, not only because the chemical mechanisms involved were not fully understood, but also because experimental techniques for detecting the low-concentration chemical species were not always available. NASA decided to focus on measuring chemical species in the atmosphere using the space-based remote sensing techniques it had developed.

Following the United Nations Conference on the Human Environment, held in Stockholm, Sweden, from June 5-16, 1972, NASA became involved in the measurement of atmospheric pollutants and greenhouse gases. At that time, it was not so much climate issues that attracted the attention of the U.S. space agency, but rather the suspected effects of pollutants emitted into the atmosphere by aircraft engines, particularly those of a hypothetical fleet of supersonic aircraft. In 1976, the U.S. Senate gave NASA responsibility for U.S. stratospheric ozone research programs. This led to the creation of the "Upper Atmosphere Research Program"[301] headed by Sir Robert Watson, a British specialist in chemical kinetics who had immigrated to the United States. The program had three components: the use of mathematical models, the study of photochemical processes, and the laboratory quantification of chemical kinetic processes.

In the early 1980s, air pollution became a global problem, and NASA launched a new program to understand chemical processes in the troposphere and their effects on the biosphere, stratosphere, and climate. Because satellites have difficulty detecting chemical species in the lower layers of the atmosphere,

[301] Upper Atmosphere Research Program or UARP.

measurements were made from airborne platforms. The Global Tropospheric Experiment was led by atmospheric chemist Robert "Joe" McNeal. Prior to joining the space agency, McNeal worked for more than a decade at the Aerospace Corporation in Santa Monica, California, and then for several years at the National Science Foundation (NSF) in Washington, DC. He was uniquely qualified to define program goals, identify the best experimenters, and organize measurement campaigns. McNeal was assisted by ecologist Robert Curtis Harriss (1941-2021), who was interested in biogeochemical interactions between the atmosphere and the biosphere.

At that time, the only instruments available to characterize the chemical composition of the atmosphere from aircraft were those that measured (with low temporal resolution) ozone, carbon monoxide, and a few greenhouse gases. But no airborne instrument was capable of systematically measuring short-lived compounds such as nitrogen oxides, volatile organic compounds, and free radicals such as OH and HO_2. McNeal's challenge was to deploy compact instruments in an airborne laboratory that could crisscross the planet and accurately measure the concentration of all chemical species. New instruments were built at several universities and research centers before being tested on preliminary flights aboard NASA aircraft between 1983 and 1989. The instruments were then used to systematically measure chemical species in different parts of the world: on the one hand, in the Atlantic and Pacific basins of the Southern Hemisphere, which are not very polluted, and on the other hand, downstream of polluted regions, especially in Asia. The goal of these various observing campaigns was to understand photochemical mechanisms in different environments and the importance of intercontinental transport of gases and aerosols. For example, the goal was to better quantify ozone production and destruction mechanisms in the troposphere, far from pollution sources. A special effort was made to measure the hydroxyl radical in unpolluted air masses to better determine its contribution to the destruction of pollutants on a global scale.

Other airborne experiments were dedicated to the measurement of emissions of biogenic compounds, the dispersion of these constituents in the boundary layer of the atmosphere, and the exchange of these species with the surface or free troposphere, mainly in tropical (Amazon) and polar regions characterized by very different photochemical and meteorological conditions. These projects were initiated to study the extent to which the biosphere regulates the chemical composition of the atmosphere at different spatial scales. Other airborne expeditions were designed to estimate the influence of forest and savannah fires, which are particularly intense in tropical regions during the dry season.

In Europe, between 1983 and 1991, measurements of chemical compounds were made from a *Caravelle* aircraft operated by the *Centre des Essais en Vol de Brétigny* in France. The person in charge of these missions was Alain Marenco, a scientist at the Centre National de la Recherche Scientifique (CNRS), based at the *Laboratoire d'Aérologie* in Toulouse. The first missions were devoted to the study of atmospheric photochemistry in West Africa, highlighting the effects of savannah fires on the chemical composition of the troposphere in this region.

The *Caravelle* then flew from the Arctic to the edge of Antarctica, following the coasts of America and Africa. These "north-south slices" provided a relatively global view of the chemical composition of the troposphere, highlighting hemispheric and seasonal differences and, in particular, the higher concentrations of ozone and its precursors north of the equator.

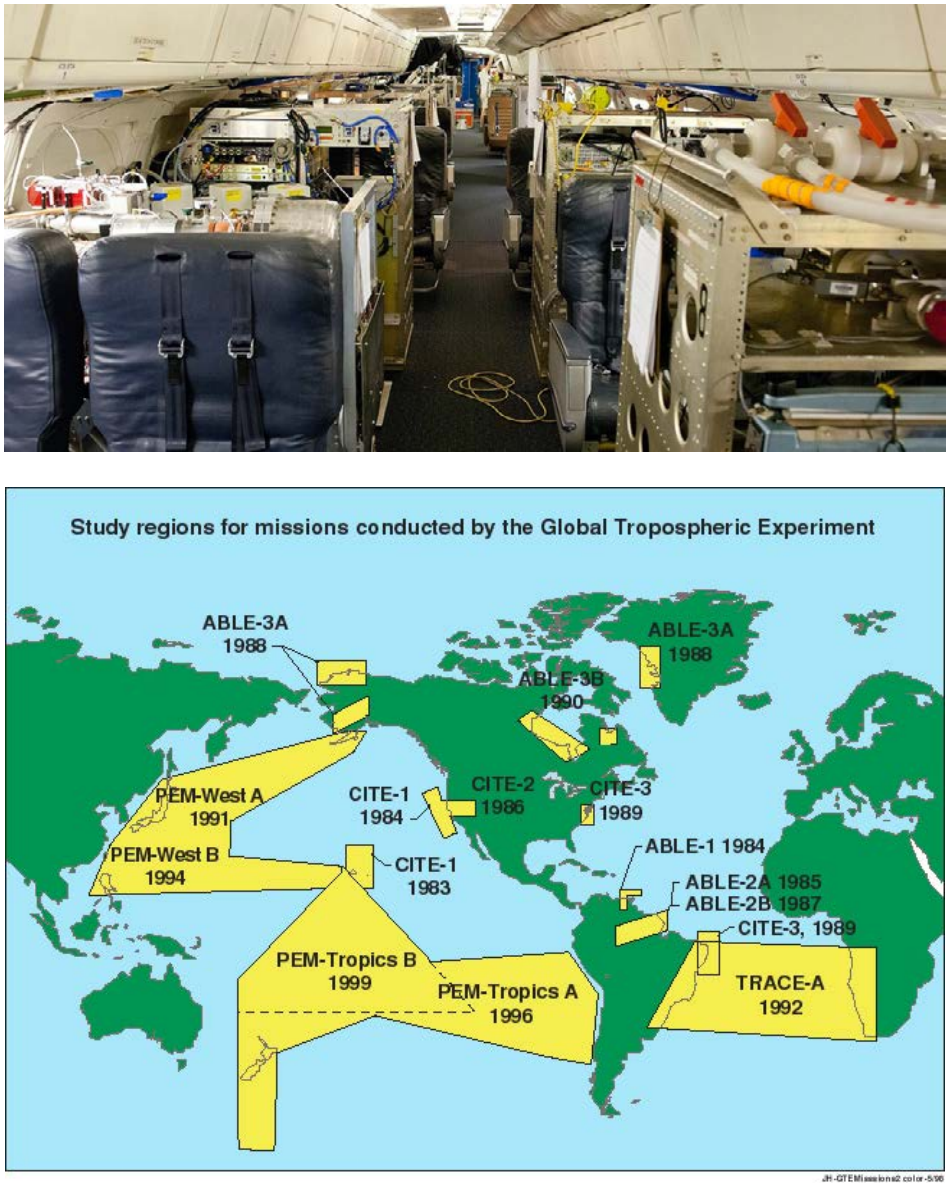


FIGURE 8.11: Top: Photograph of an aircraft cabin equipped with various measuring instruments. Bottom: Regions of the world where measurements of chemical species concentrations have been made from NASA aircraft. Source: NASA.

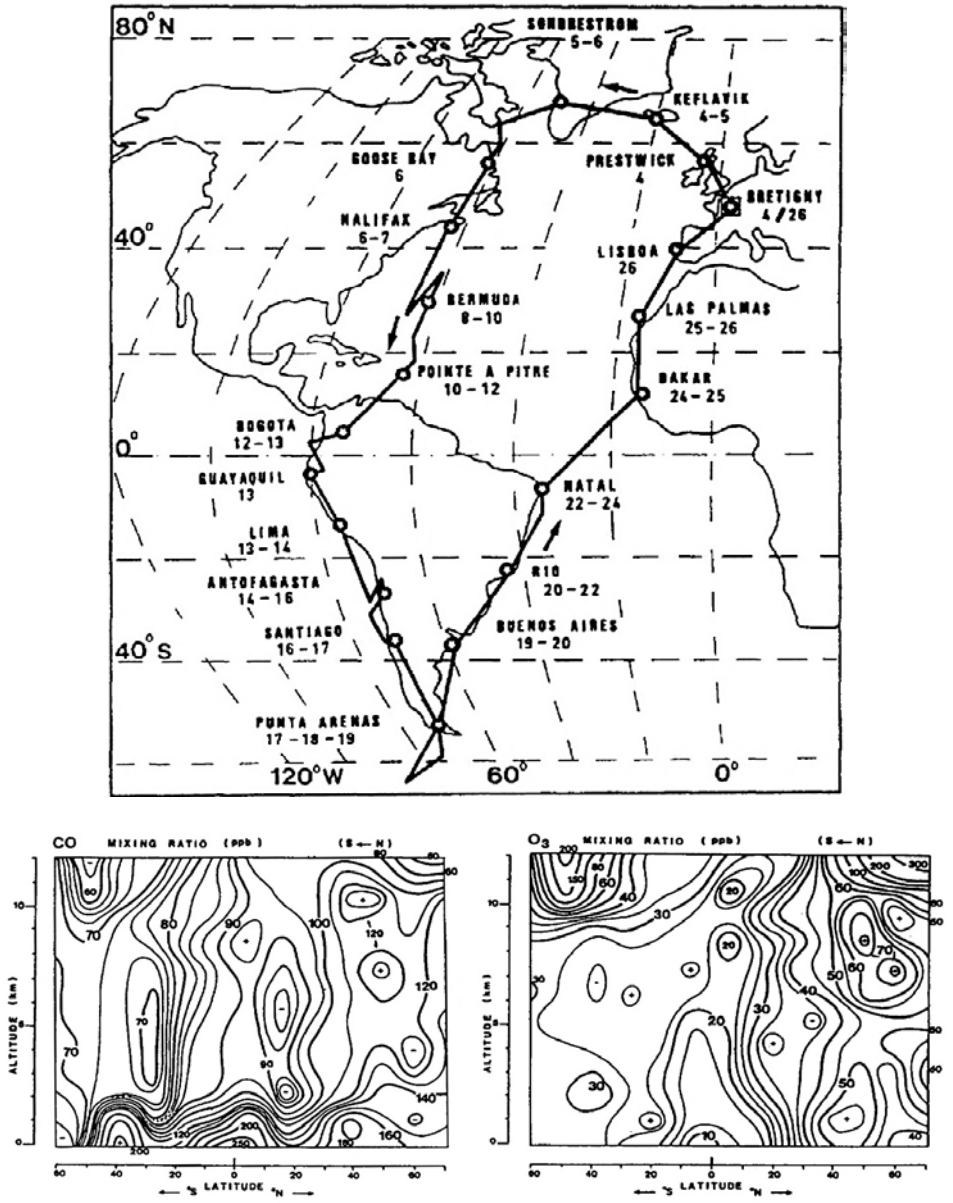


FIGURE 8.12: Top: Route taken by the Caravelle-116 during the STRATOZ III campaign between June 4 and 26, 1984. Bottom: meridian distributions of carbon monoxide and ozone deduced from observations made from the aircraft as it flew from the northern to the southern hemisphere. Ten thousand ozone measurements and two thousand carbon monoxide and methane measurements were taken over the course of 21 flights during the campaign. Forty-two vertical profiles of these constituents were obtained during the aircraft's ascent and descent. Source: Marenco, A. Large scale distributions of O_3, CO and CH_4 in the troposphere from scientific aircraft measurements (STRATOZ III), *in* Isaksen, I.S.A. (ed.), *Tropospheric Ozone, Regional and Global Scale Interactions*, Reidel Publishing Company, Dordrecht, 425 pp., 1987.

After 1998, the experiments with the French aircraft were followed by the implementation of a Franco-German project called MOZAIC[302]. In this new phase, several scheduled Airbus 340 aircraft were equipped with instruments to measure ozone and water vapor concentrations, and later carbon monoxide and nitrogen concentrations, between 0 and 12 km altitude, mainly near the tropopause (8 to 12 km). This program made it possible to establish a climatology of chemical species in regions regularly traveled by aircraft, and to obtain quasi-vertical profiles of these species in regions close to cities where aircraft landed and took off.

Laboratory aircraft have one major advantage: they collect highly accurate information on the atmospheric abundance of a large number of chemically interacting compounds, allowing *in situ* verification of hypotheses formulated about photochemical processes studied in the laboratory. However, the use of airborne platforms also has a disadvantage: measurements are limited to the few geographical regions crossed by the aircraft. It is therefore useful to simultaneously deploy instruments on satellites that have a much wider geographical coverage, even if information on the vertical distribution of chemical species is often sketchy. Most satellites with sensors pointed at the Earth's surface observe only the "column" of chemical species, i.e., their vertically integrated concentration between the ground and the space-based sensor. Thus, measurements from laboratory aircraft and satellites, plus the contribution of instruments installed on the ground or carried by sounding balloons, provide complementary information that is essential for a detailed analysis of chemical processes in the atmosphere.

The first space programs focused on the measurement of chemical species present in the stratosphere, which are easier to detect than chemical species present in the lower layers of the atmosphere. Indeed, the presence of clouds and the high concentration of water vapor are two factors that make it difficult to detect trace species at low altitudes. Later, in 1981, and again in 1984 and 1994, Henry G. Reichle of NASA's Langley Research Center in Virginia placed a filter radiometer aboard the Space Shuttle to measure carbon monoxide (CO) in the troposphere. His measurements revealed the high concentrations of CO in the tropics during the dry season, when forest and savanna fires are common.

Since the late 1990s, with the launch of NASA's Terra, Aqua, and Aura satellites, a number of orbiting instruments have measured tropospheric concentrations of carbon monoxide (MOPITT, AIRS, and TES), nitrogen oxides (OMI), ozone (AIRS and OMI), sulfur dioxide (OMI, TES), and aerosols (MODIS), with varying degrees of success. MOPITT, for example, has been measuring carbon monoxide for more than twenty years and has been able to observe long-term trends resulting from human activities as well as more sporadic disturbances caused, for example, by gigantic forest fires. Other space missions, often of European origin, have been based mainly on the GOME, IASI, and TROPOMI instruments. The latter have allowed additional observations, sometimes with better spatial resolution, and the detection of other

[302] Measurement of Ozone by Airbus In-service Aircraft.

species such as formaldehyde or ammonia. The TROPOMI satellite measures nitrogen oxides and other coumponds with a spatial resolution of a few kilometers and thus detects urban and industrial sources of these chemical species on a global scale. In recent years, geostationary satellites such as GEMS and TEMPO have observed the diurnal variation of several chemical species over specific regions.

Mathematical Models of Tropospheric Chemistry

The work of Hiram Levy II mentioned above was of great interest to Paul Crutzen. This prominent scientist decided to extend the stratospheric model he had developed in the late 1960s to the lower atmosphere and include the photochemical processes that lead to the formation of the ozone molecule below the tropopause. This work was presented at the Quadrennial Ozone Symposium in Arosa, Switzerland, in 1972, but at the time received little attention because scientists were more concerned with the possible destruction of the stratospheric ozone layer in response to human activities. Crutzen continued his modeling work, however, in collaboration with Jack Fishman and Susan Solomon at the *National Center for Atmospheric Research* in Boulder, Colorado.

Given the limited computing capacity available at the time, these early models were necessarily simplified; they were limited to calculating the vertical distribution of the chemical compounds, without providing any information on the variations that exist as a function of latitude and longitude, and therefore as a function of time of day. The first attempts to represent tropospheric ozone in three dimensions were made in the early 1980s at the *Max Planck Institute for Chemistry* in Mainz, Germany, where Crutzen had just been appointed director and was now working with Peter Zimmermann. At the *Institut d'Aéronomie Spatiale* in Brussels, Belgium, a similar model was developed by Jean-François Müller. A few years later, more comprehensive global models directly coupled to meteorological models were developed, notably at NCAR and Harvard University. Daniel Jacob and his group at Harvard University studied in detail the observations made by NASA aircraft, and their interpretation made it possible to quantify more precisely the role of various chemical mechanisms that were still poorly understood. The NCAR model became the "chemical component" of the Earth System Model developed by the American scientific community.

These global models, which are now powerful enough to handle several hundred interacting chemical compounds simultaneously with a spatial resolution of a few tens of kilometers, take into account various processes: natural and anthropogenic emissions of primary compounds, mass transport on different spatial scales, photochemical reactions that produce and destroy various chemical compounds, the deposition of molecules and aerosols on the Earth's surface, and the "scavenging" of soluble species by precipitation. Analogous models that apply to a specific geographic region, but with a spatial resolution of a few kilometers, can treat the various atmospheric processes in more detail.

These regional models require conditions, often borrowed from global models, to be specified at the lateral boundaries of the spatial domain under consideration. To overcome this limitation, hybrid models are now available that cover the entire planet but allow increased spatial resolution in a particular region of the Earth.

Simulations of atmospheric composition can be performed by numerically solving the equations of atmospheric dynamics and chemistry, but it is sometimes desirable to constrain the solution of these equations by information provided by measurements, for example, from aircraft or satellites. In such cases, observational data are *assimilated* using a number of optimization techniques that are now well established. Inverse modeling can also be used to constrain emissions of chemical compounds so that they are consistent with experimentally measured atmospheric concentrations.

Atmospheric models are powerful tools for predicting air quality on a global or regional scale and are therefore increasingly used operationally by weather services. For example, the European *Copernicus* program, coordinated by the *European Centre for Medium-Range Weather Forecasts* (ECMWF), publishes a daily global forecast of air chemistry for the next five days.

Increasingly, scientific questions are being asked about the physical and biogeochemical interactions between the different planetary compartments: the atmosphere, the continental surface, and the ocean. For this reason, atmospheric models are sometimes incorporated into a more comprehensive model of the Earth system. These models include a representation of the phenomena occurring in the atmosphere (dynamics, chemistry), the ocean (circulation, biogeochemistry), the continental biosphere (ecosystem productivity), the cryosphere (ice thermodynamics and dynamics), as well as the physical and chemical interactions that exist between these different compartments of the Earth system. The models that consider the impact of human activities (emissions of pollutants and greenhouse gases, changes in ecosystems, disturbances to the hydrological cycle, etc.) allow us to reproduce past trends and project future developments in the climate and, more generally, in the terrestrial environment. Artificial intelligence techniques involving data-based training are increasingly being used to derive global and regional distributions of atmospheric chemical species.

International Cooperation

At the end of the 1980s, solving the problem of air pollution on a global scale became a scientific and political priority. The scientific communities of several countries were mobilized. In the United States, three science administrators helped organize and structure the research effort: Robert W. Corell, Assistant Director for geophysics at the National Science Foundation (NSF), Shelby G. Tilford (1937-2022), Associate Administrator for NASA's Mission to Planet Earth, and J. Michael Hall, Director of the Office of Global Programs at the National Oceanic and Atmospheric

Administration (NOAA)[303]. The objective of these three colleagues was to develop a comprehensive and holistic program on global change and, in particular, to include elements related to atmospheric chemistry and climate. At the same time, a group of scientists led by Ralph Cicerone, Ronald Prinn, and Robert Duce developed a program called the "Global Tropospheric Chemistry Program," which served as a framework for activities supported by the three U.S. research agencies. Atmospheric chemist Jarvis L. Moyers (1943-2011) was responsible for the implementation of this project at NSF.

But it was in Australia that an important event took place from November 7 to 11, 1988. At Dookie College in the province of Victoria, a group of about fifty scientists from around the world met to address a challenge and respond to the following questions: how to quantitatively understand the chemical and physical properties, as well as the biological processes, that determine the composition of the atmosphere? And how can this knowledge be used to study the past evolution and project the future evolution of the Earth's atmosphere?

The Dookie campus, which houses a school specializing in agriculture, is located in an area completely isolated from the rest of the world and therefore conducive to reflection and planning of research activities. Several keynote speeches, given by leading scientists, set out the scientific stakes of the meeting and highlighted the challenges that research must address: the relationship between trace gases and climate, the relationship between aerosols and climate, ozone and the oxidizing capacity of the troposphere, hydrocarbons in the atmosphere, perturbations in the nitrogen cycle, and interactions between the biosphere and the troposphere.

The discussions were constructive and demonstrated the importance of establishing an international program to address the growing concern about changes in the composition of the atmosphere and their potential impact on humankind. This program, called the International Atmospheric Chemistry Project (IGAC), while focusing on atmospheric composition and chemistry, recognizes that the atmosphere, oceans, land surfaces, and biosphere form an interactive system that together determine the global environment and its susceptibility to change.

The overall goal of IGAC is to measure, understand, and predict changes in the chemical composition of the global atmosphere, particularly the oxidizing power of the atmosphere, the effects of atmospheric composition on climate, and the interactions of chemical species with living matter. Among the topics selected, the initial program focused on increasing acidity of precipitation, stratospheric ozone depletion, greenhouse warming, and biological damage caused by increasing levels of oxidants in the atmosphere. Over the years, IGAC has become the international reference project for researchers working on global atmospheric chemistry issues, involving observations of atmospheric chemical constituents, laboratory measurements of chemical kinetics, and mathematical models that simulate chemical processes and cycles.

[303] Robert Corell, Shelby Grant Tilford, J. Michael Hall and Aristides A. N. Petrinos, Director of the U.S. Department of Energy's Office of Biological and Environmental Research, and Jack D. Fellows, Unit Chief in the White House Office of Management and Budget, founded and developed the U.S. Global Change Research Program (USGCRP).



FIGURE 8.13: The "founding fathers" of the International Atmospheric Chemistry Project (IGAC) at the founding meeting (November 7-11, 1988) at Dookie Agricultural College, 215 km north of Melbourne, Australia. From left to right: E. Sanhueza (Venezuela), Daniel Albritton (USA), Robert Duce (USA), Ian Galbally (Australia), Paul Crutzen (Germany), Dieter Ehhalt (Germany), Patrick Buat-Menard (France) and Henning Rodhe (Sweden). The table in the fonds shows IGAC's scientific priorities (Source: Henning Rodhe and Rolf Müller).

9
Airborne Particles

In 582 CE, the historian Gregory (~538-594), bishop of the city of Tours in France, reported in Book 6 of his *Stories*:

> "In the territory of Paris, a veritable rain of blood fell from the clouds: many people received it on their clothes, and it stained them with such stains that they stripped off their clothes in horror. The same miracle occurred in three places in the territory of this city."

Such showers of color have been mentioned several times over the centuries: in Tours (France) in 754, in Hungary in 765, in Dinkelsbühl (Germany) in 1554, in Genoa (Italy) in 1744, in Aix-en-Provence (France) in 1606, in Naples (Italy) in 1813, and in Palermo (Italy) in 1901, to name a few. These events were generally considered to be punishments inflicted on people or omens of painful events. As early as the sixth century BCE, Homer alluded to them in the *Illiad*, attributing these meteorological events to the action of Zeus. As for the poet Cicero, he thought it was rather "a contagion of terrestrial origin[304]". But wasn't this God's punishment, since the death of Pope Adrian II on December 14, 872, was preceded by three days of bloodshed in Brescia, Italy? In any case, for Gregory of Tours, these natural events were a warning from heaven with painful consequences for the population:

> "This year there was a great mortality among the people: various very dangerous diseases, and accompanied by pustules and blisters, caused the death of a large number of people."

However, this viewpoint changed in the nineteenth century. The chemical analyses available today show that these blood showers are made up of water droplets containing significant amounts of mineral elements or organic substances. We now know that these colored precipitations are associated with the dispersal of desert sand dust, seaweed spores, or volcanic particles.

Air is not a fluid composed only of substances in the gaseous state; in addition to the familiar water droplets, it contains a wide variety of small solid or liquid objects suspended in the air, whose properties and sizes (from a few nanometers to a few hundred micrometers) vary widely. These particles are called

[304] "ex aliqua contagione terrena".

aerosols, a term introduced during World War I by the Irish chemist Frederick George Donnan (1870-1956). One generally distinguishes hydrometeors (i.e., raindrops, ice crystals, etc.) from aerosols (i.e., smaller particles that remain suspended in the air for longer periods of time).

Any material that breaks down into tiny particles can be injected into the atmosphere. The largest of these particles, however, do not remain in the atmosphere for long; under the influence of gravity, they quickly fall back to Earth. On the other hand, the smallest particles remain in the air for several days or even weeks if they are injected or transported into the upper layers of the troposphere. If they enter the stratosphere, they remain there for several years. The quantities of mineral particles carried by winds are considerable; dust grains from deserts or arid zones, with fragments of quartz, limestone, and gypsum, are injected into the atmosphere. It was the American geologist William Phipps Blake (1827-1910) who first pointed out that the presence of mineral dust in the air is due to the superficial disintegration of rock or soil by the process of erosion, thus challenging the idea - generally accepted at the time, notably by the astronomer François Arago (1786-1853) - that these fine particles were mainly of cosmic origin. Another source of natural aerosols is the decomposition of plant and animal matter and pollen. Salt particles from sea spray and soot particles from forest fires should also be considered. A major source of atmospheric particles is also associated with volcanic activity. During explosive eruptions, these particles can be injected into the upper layers of the atmosphere before being dispersed on a large scale and orbiting the Earth several times. In addition to these naturally occurring particles, some result from human activities such as the combustion of wood, oil, and gas (power generation, home heating, automotive, marine, and air transportation), as well as from various agricultural and industrial operations.

Primary particles are those emitted directly into the atmosphere. *Secondary* particles are formed *in situ* by the physicochemical transformation of gaseous precursors in the air, such as sulfur dioxide (SO_2), nitrogen oxides (NO, NO_2), and certain organic molecules. The largest particles are generally of natural origin, while a significant fraction of the smallest particles are the result of both anthropogenic emissions and oxidation or condensation of precursor gases.

Aerosol size is an important parameter in the study of atmospheric aerosols. In the 1960s, Kenneth T. Whitby (1925-1983), a professor at the University of Minnesota and a member of the U.S. National Academy of Engineering, developed an experimental technique for measuring submicron particles. He classified atmospheric aerosols into three size modes: the nucleation mode (0.015 to 0.04 μm) that contains newly formed particles; the accumulation mode (0.15 to 0.5 μm) that contains particles that result from gas condensation and coagulation[305]; and finally, the mode that refers to large particles (5 to 30 μm). Air pollution studies often refer to particles according to their aerodynamic diameter, introducing the terminology of "particulate matter" (*PM*): particles with a diameter of less than 10 μm are referred to as PM_{10}, while those with a diameter of less than 2.5 μm are called $PM_{2.5}$. Particles smaller than 1 μm are labeled

[305] The process by which small particles come together to form a larger particle.

PM_1, and ultrafine particles are those with a diameter no larger than 0.1 μm. The finest particles are particularly harmful to health because they penetrate deep into the respiratory tract and even the bloodstream.

Particles are also distinguished according to their physicochemical properties. The atmosphere contains soluble *inorganic particles*, such as nitrates, sulfates, and sea salts; insoluble particles, such as mineral dust; and carbonaceous particles, such as soot. The latter, composed almost entirely of carbon atoms, are produced by the incomplete combustion of fossil fuels or biomass. *Organic particles* generally contain carbon, hydrogen, and oxygen atoms, and often nitrogen. They may be emitted directly into the atmosphere or may result from the oxidation of volatile organic compounds emitted by vegetation or from human activities. In addition to these particles of terrestrial origin, there is also dust from space that contains metals of meteoric origin (iron, magnesium,

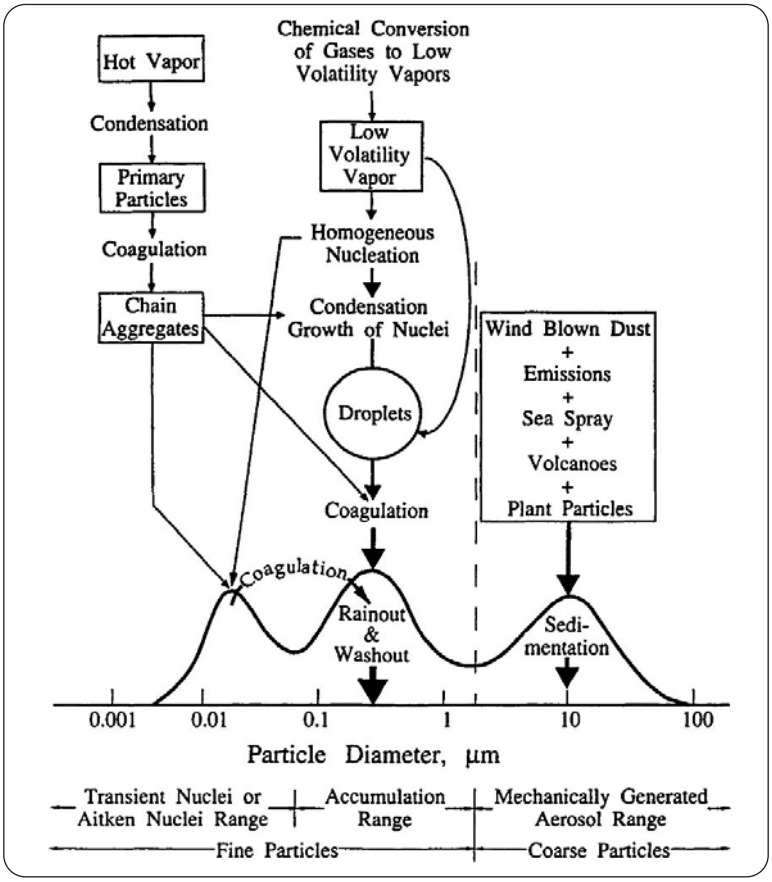


FIGURE 9.1: Size distribution of atmospheric aerosol with nucleation mode (Aitken nuclei), accumulation mode and large aerosols. Particle formation (nucleation) and transformation (coagulation) processes are shown. Source: D. Charpin *et al*, *Journal of Respiratory Diseases*, ***33***(6) 484-508, 2016. Based on Witby, K.T., Cantrell, B., *Proc. International Conf. on Environ. Sensing and Assessment, Institute of Electrical and Electronic Engineers*, 1976.

silicon, sodium, and, to a lesser extent, calcium and potassium). These metals are mainly observed between 80 and 105 km altitude. They have been the subject of interesting studies by upper atmosphere specialists.

Work carried out during the twentieth century has shown that human activities are responsible for a significant fraction of atmospheric particles, especially in industrial and urban areas. These particles, which are generally acidic, can be transported by winds and deposited on vegetation; they were responsible for significant damage to forests in Europe and North America during this period. Today, efforts to improve air quality focus on reducing atmospheric concentrations of these particles, which are harmful to health and are responsible for several million premature deaths worldwide each year. Finally, some aerosols, such as sulfates, scatter some of the incoming sunlight back into space, cooling the Earth's surface and thus influencing climate. Other aerosols, such as soot particles, which can absorb infrared radiation, warm the surface.

It has taken several centuries to establish the properties and understand the role of aerosols in the atmosphere. We briefly summarize how knowledge in this field has progressed throughout history.

The First Ideas

Since ancient times, philosophers and naturalists have been interested in the airborne particles produced by sandstorms and forest fires, one of whose effects is to reduce visibility. Where do these fine particles in the atmosphere come from? In 1700, French chemist and apothecary Nicolas Laméry (1645-1715) thought that he knew the answer. In a paper presented to the *Académie Royale des Sciences*, he offered some interesting insights. For this scholar, contemporary of King Louis XIV and author of a remarkably clear "*Cours de Chymie*" (1675), the atmosphere is subject to "sulfurous winds" produced during earthquakes. According to Laméry:

> "Earthquakes are apparently caused by a vapor which, after being produced by the violent fermentation of iron and sulfur, has been converted into a sulfurous wind, which makes its way through and rolls wherever it can. [...] If it finds a few openings to get out, it rushes forward with great impetuosity, and this is what we call a hurricane. [...] For this wind, which contains exalted sulfur, becomes entangled in the clouds and, being strongly beaten and compressed there, acquires a movement great enough to ignite and form lightning."

This argument was used by the philosopher Immanuel Kant (1724-1804) to explain the fog that covered much of Europe after the Lisbon earthquake of 1755. Kant referred to the exothermic conversion of sulfates to sulfuric acid, which would then be released into the atmosphere. Thus, the particles observed in the atmosphere would be composed of sulfur.

A thick fog that lasted for several months was once again observed in Europe, this time in 1783. Was this specific atmospheric situation due to the series of five earthquakes that struck Calabria in the Kingdom of Naples in February and March of that year? Not according to Jacques Antoine Mourque de Montredon (1734-1818),

a French naturalist and politician[306] during the tumultuous French Revolution. Mourque de Montredon took up the idea expressed almost a century earlier by Laméry: for him, the dry fog that covered Europe from Iceland to Portugal and from North Africa to Syria, and was observed as far away as Labrador, was explained by the presence of sulfur particles stagnant in the air[307]. The particles that made up this haze did not come from earthquakes but had been injected into the atmosphere during volcanic eruptions. Such geophysical events occurred in Iceland during this period: first, the eruption of the *Nyey* volcano, observed by fishermen in March 1783, when an island formed in western Iceland; second, the gigantic eruption of the *Laki* volcano, which began on June 8, 1783[308], and which, according to recent estimates, released 122 megatons of sulfur dioxide (SO_2) into the atmosphere and over 200 megatons of particles composed of sulfuric acid (H_2SO_4) and water[309]. The resulting layer of aerosols reached an altitude of 13 km and was dispersed throughout the upper troposphere and lower stratosphere. The consequences of this eruption were devastating, with more than half of Iceland's livestock wiped out and extreme weather phenomena occurring throughout Europe and North America. The following winter was particularly harsh, with temperatures averaging 1.3 °C below climatological values. The French scientist's view of the role of volcanoes was supported by the German physicist Christian Gottlieb Kratzenstein (1723-1795), professor at the University of Copenhagen, by the Swiss naturalists H. Guerin and Johan Rudolf von Salis-Marschins, by the Belgian botanist Eugène-Joseph d'Olmen de Poederlé (1742-1813), and by an influential politician, Benjamin Franklin (1706-1790), who was the diplomatic representative of the United States in France at the time.

Franklin was intrigued by the persistence of the fogs observed in Europe, and in a 1784 letter to his friend Thomas Percival (1740-1808), a Manchester physician, he described the phenomenon[310]:

> "During several of the summer months of the Year 1783, when the effect of the Sun's rays to heat the Earth in these northern regions should have been

[306] Jacques Antoine Mourque de Montredon was a Huguenot whose family fled to Montpellier in southern France, fleeing the Catholic Church's Inquisition. He was Minister of the Interior for five days (June 13-18, 1792), less than two months before the abdication of King Louis XVI.

[307] de Montredon, M. M., Recherches sur l'origine & sur la nature des Vapeurs qui ont régné dans l'Atmosphère pendant l'été de 1783, *Mem. Acad. R. Sci., Paris*, MDCCLXXXI, 754-773, 1784.

[308] The fissure created by the eruption of the Laki volcano was only discovered in 1794 by Icelandic naturalist and physician Sveinn Pálsson (1762-1840).

[309] Demarée, G.R., Ogilvie, A.E.J., Zhang, D., Further evidence of Northern Hemispheric coverage of the Great Dry Fog of 1783. *Climate Change*, **39**, 727-730, 1998. Thordarsonand T., Self, S., Atmospheric and environmental effects of the 1783-1784 Laki eruption: A review and reassessment. *Journal of Geophysical Research, 108*, 4011, 2003, https://doi.org/10.1029/2001JD002042.

[310] "Meteorological Imaginations and Conjectures, [May 1784]," *Founders Online,* National Archives, https://founders.archives.gov/documents/Franklin/01-42-02-0184. [Original source: *The Papers of Benjamin Franklin,* vol. 42, *March 1 through August 15, 1784*, ed. Ellen R. Cohn. New Haven and London: Yale University Press, 2017, pp. 289–294.]

> greatest, there existed a constant fog over all Europe, and great part of North America. This fog was of a permanent nature; it was dry, and the rays of the Sun seemed to have little effect towards dissipating it, as they easily do a moist fog arising from water."

He suggested two possible causes for these dry fogs: first, the penetration of a meteor into the atmosphere, which had been observed along the coasts of Scotland and England, then over France and northern Italy; and second, the emission of dust from one of the volcanoes that had awakened in Iceland during the year.

> "The cause of this universal fog is not yet ascertained. Whether it was adventitious to this Earth, and merely a smoke proceeding from the consumption by fire of some of those great burning balls or globes which we happen to meet with in our rapid course round the Sun, and which are sometimes seen to kindle and be destroyed in passing our atmosphere, and whose smoke might be attracted and retained by our Earth. Or whether it was the vast quantity of smoke long continuing to issue during the summer from *Hecla* in Iceland, and that other volcano which arose out of the sea near that Island; which smoke might be spread by various winds over the northern part of the world; is yet uncertain."

The following winter was particularly harsh in Europe and North America, with heavy snowfalls and flooding after the ice melted. The winter conditions were so bad that it was difficult to gather enough members of the U.S. Congress in Annapolis to ratify the Treaty of Paris, which ended the Revolutionary War between England and the United States. Once the peace treaty was ratified, the emissaries had difficulty crossing the Atlantic to exchange the adopted document with the British after their military defeat.

Perhaps the most interesting aspect of Franklin's writings is that he linked low winter temperatures to volcanic eruptions, suggesting for the first time a possible effect of atmospheric particles on the Earth's climate. In a memoir dated May 1874, he wrote

> "It seems however worth the inquiry, whether other hard winters, recorded in history, were preceded by similar permanent and widely extended summer fogs. Because, if found to be so, men might from such fogs conjecture the probability of a succeeding hard winter, and of the damage to be expected by the breaking up of frozen rivers in the spring; and take such measures as are possible and practicable, to secure themselves and effects from the mischiefs that attend the last."

Two years later, on December 17, 1786, Jane Mecom (1712-1794), Franklin's younger sister and confidante living in Boston, congratulated her brother:

> "Your predictions concerning a hard winter are beginning to be verified in a formidable manner."

A century later, dry fog was again observed, this time following the explosive eruption of Krakatoa in Indonesia in August 1883. The German meteorologist Johann Kiessling (1839-1905) attributed the magnificent sunsets that followed the eruption to the diffraction of light by particles and clouds of dust produced

by the volcano. He hypothesized that the material ejected into the atmosphere contained large amounts of sulfuric gas. However, it wasn't until the eruption of Mount Agung in Bali in 1963 that it was fully recognized that volcanic aerosols are composed primarily of sulfuric acid droplets. Measurements taken since 1785 showed that particles are present in the air even in the absence of violent geophysical phenomena.

It was not until the advent of experimental science that more systematic studies could be carried out. For example, beginning in 1868, John Tyndall (1820-1893), known for his laboratory work on absorption by greenhouse gases, conducted a series of experiments in Dublin in which he produced dust clouds in a glass tube after exposing vapors of volatile liquids to light. This work highlighted the importance of photochemistry in aerosol formation processes. Tyndall wrote in 1881:

> "With regard to size, there is probably no sharp line between molecules and particles; the one gradually shades into the other. But the distinction that I draw is this: the atom or molecule, if free, is always part of a gas, the particle is never so. A particle is a bit of liquid or solid matter, formed by the aggregation of atoms or molecules."

In the United States, physicist Carl Barus (1856-1935), who spent most of his career at Brown University, made the first systematic long-term measurements of particle concentrations in the atmosphere. The son of a German immigrant, who received his Ph.D. from the University of Würzburg in Germany and was later elected to the U.S. Academy of Sciences, Barus developed a "condensation chamber" that allowed him to determine the number of dust grains contained in an air-filled enclosure using a method known as expansion[311]. It was Barus who first used the term "nucleation" to describe the initial process by which small nuclei are formed.

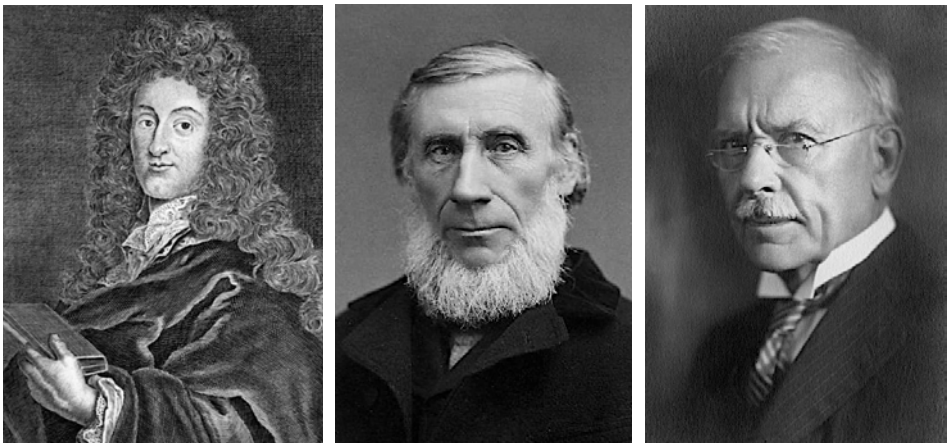


FIGURE 9.2: Nicolas Laméry, John Tyndall and Carl Barus.

[311] In such a chamber, supersaturated water vapor condenses on aerosol particles, and the resulting water droplets are photographed under a microscope. The number of droplets can then be counted and the aerosol concentration determined.

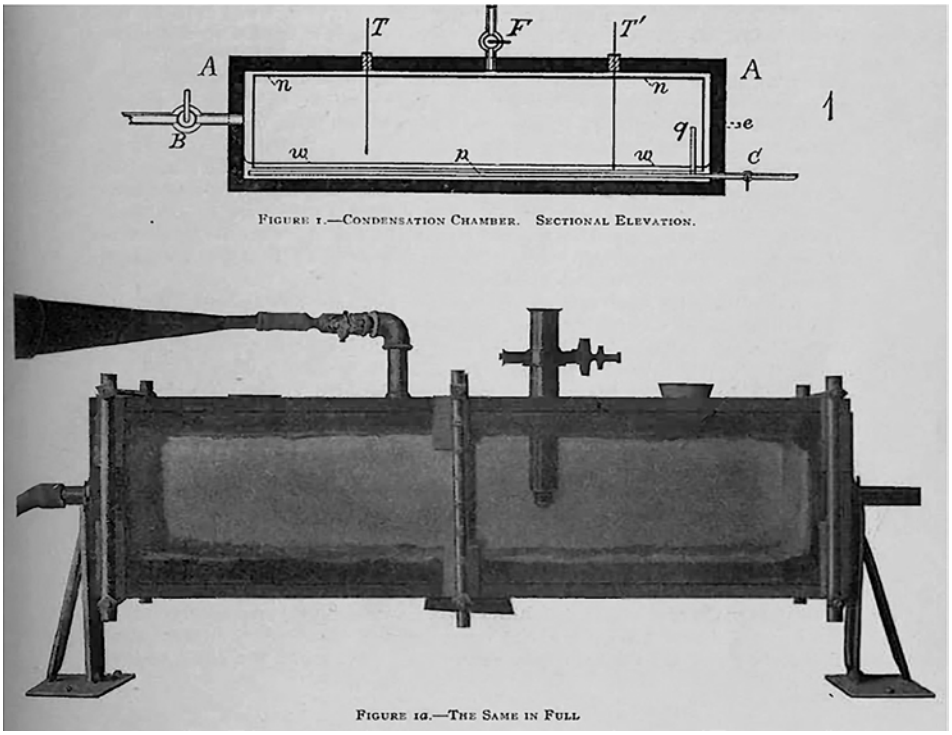


FIGURE 9.3: Condensation chamber for measuring atmospheric particles. Source: Barus, C., A Continuous Record on Atmospheric Nucleation. Smithson. *Contrib. Knowl. 34,* 1905.

Particles and Microbes

However, one question had long been asked: Can fine particles suspended in the air carry over long distances living microorganisms, including viruses, bacteria, and fungi, whose pathogenic properties would pose a threat to public health? The first answers to these questions were provided by Christian Gottfried Ehrenberg (1795-1876). This Saxon-born naturalist, a distinguished member of the Royal Prussian Academy of Sciences, was one of the first to study the microscopic compounds contained in grains of atmospheric dust. In 1829, he accompanied Alexander von Humboldt on a journey across Russia to the borders of China. He brought back samples of dust, which he examined closely and discovered the presence of living microorganisms. What was their origin? And did this discovery prove that there exists in nature a process of spontaneous generation (without ascent) of life from inanimate matter? This thesis, which goes back to the pre-Socratic philosophers and was supported by Aristotle, was taken up again in the nineteenth century by the English biologist Abbot John Needham[312] (1713-1781)

[312] Canon, first director of the *Académie Impériale de Bruxelles*, member of the Royal Society.

but was challenged by another priest, the Italian biologist Lazzaro Spallazani (1729-1799). It was finally invalidated by the independent work of the English naturalist Charles Darwin and the French microbiologist Louis Pasteur.

Charles Darwin (1809-1882), best known for his theory of evolution, believed that all living species evolve through the natural selection of small hereditary variations that increase an individual's ability to compete, survive, and reproduce[313]. Between 1831 and 1836, he made a voyage around the world aboard a Royal Navy ship, the *Beagle*, with future Vice-Admiral Robert FitzRoy at the helm. The two men, though very different in character, got on well and worked well together, although the captain suffered from occasional bouts of depression. While sailing along the African coast, Darwin collected samples of dust, small particles that had been generated by sandstorms in the nearby Sahara Desert. In his logbook, he wrote

> "On the 16th of January 1832, we anchored at Porto Praya, in St Jago, the chief island of the Cape de Verde archipelago. Generally, the atmosphere is hazy; and this caused by the falling of impalpably fine dust, which was found to have slightly injured the astronomical instruments. The morning before we anchored at Porto Praya, I collected a little packet of this brown-colored fine dust, which appeared to have been filtered from the wind by the gauze of the vane at the masthead."

The samples were sent to Christian Ehrenberg in Prussia, who analyzed them in his laboratory. They complemented those the Berlin biologist had received in 1812 from the German explorer Robert Hermann Schombrugk (1804-1865), who had collected them in the Barbados Islands. Further samples were collected in 1838 by Lieutenant Robert Bastard James (1815-1838), who sailed the Atlantic aboard the Royal Navy ship *The Spey*; they were also sent to Ehrenberg by Darwin. Initial analyses suggested that microbes adhering to dust grains could be transported over long distances.

In France, beginning in 1859, Louis Pasteur (1822-1895) also became interested in the spontaneous generation hypothesis. Born in Dole in the Jura region, Pasteur was a former student at the École Normale Supérieure in Paris. Along with Robert Koch (1843-1910) in Germany, he is often considered the father of microbiology. In 1848, Pasteur was appointed professor at the University of Strasbourg, before moving to the University of Lille in 1854, where he began his work on fermentation. In 1857, he was hired by the École Normale Supérieure, where he became director of scientific studies. Elected to the Académie des Sciences in 1862, this chemist and physicist is best known for his studies on fermentation and the development of the rabies vaccine.

Pasteur, who was very close to Emperor Napoleon III, was supporting the positivist movement that was developing in France. He opposed the concept of spontaneous generation and thus became involved in a controversy with the medical biologist Félix Archimède Pouchet (1800-1872), an ardent supporter

[313] Darwin, C., *On the origin of species by means of natural selection or the preservation of favoured races in the struggle for life,* John Murray Publisher, London, 1859.

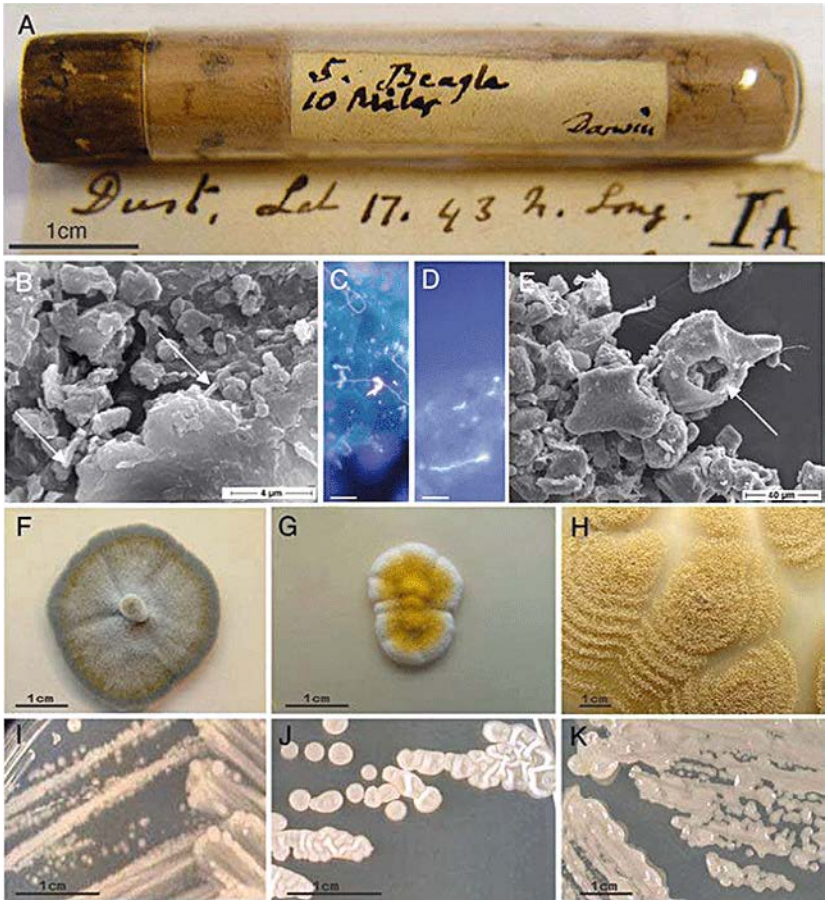


FIGURE 9.4: Sand dust from the Atlantic Ocean (17.43 N, 25.54 W), collected on March 9, 1838 (collection of the "Museum für Naturkunde", Berlin). Colonies of microbes on mineral surfaces detected by various techniques. Source: Gorbushina *et al,* Life in Darwin's dust: intercontinental transport and survival of microbes in the nineteenth century. *Environmental Microbiology,*9(12), 2911-2922, 2007.

of the theory of heterogenesis[314]. Pasteur performed a famous experiment that allowed him to reject the idea that life arises spontaneously. He boiled a meat broth in a swan-neck flask with a long, downward-curved neck. The bend in the neck prevented falling particles from reaching the broth while still allowing air to flow freely. When the flask was rotated to allow particles to fall down the bend, the broth quickly became clouded with an increasing number of microorganisms. The flask was therefore being contaminated by airborne bioparticles from the outside. The conclusion was clear. In a closed environment, where there is no contamination from the surrounding air, no life can appear. Only life begets life.

[314] Production of a living organism without the help of pre-existing organisms of the same species.

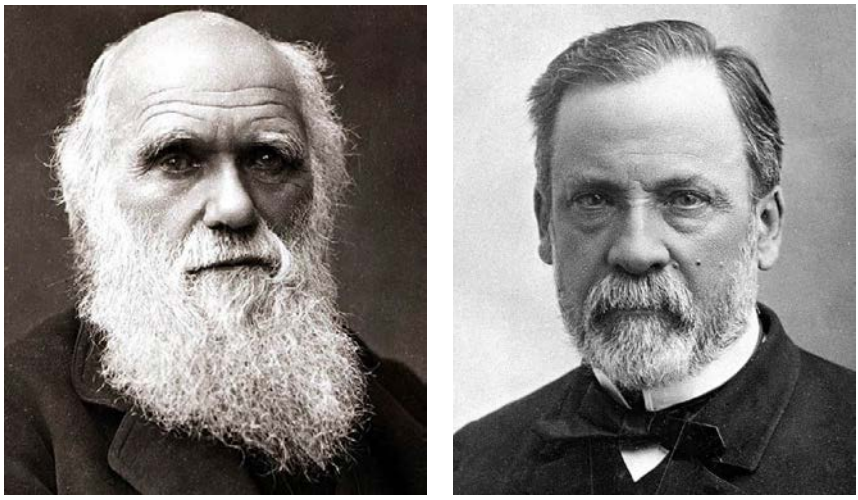


FIGURE 9.5: Charles Darwin (left) and Louis Pasteur (right).

This experiment was criticized by several contemporaries, notably Pouchet, but Pasteur's views, supported by the Paris Academy of Sciences, eventually prevailed. It was the experimental work of John Tyndall that put an end to the controversy. Although challenged in the 17th and 18th centuries by the Italian biologists Francesco Redi (1626-1697) and Lazzaro Spallanzani (1729-1799), the Aristotelian concept of spontaneous generation was not fully discredited until the mid-19th century, thanks to the work of Paster and Tyndall.

Despite this experimental evidence, the debate was not over. Systematic studies of atmospheric dust were conducted at the Parc Montsouris Observatory in Paris by aerobiologist Pierre Antonin Miquel (1850-1922), a pharmacist and physician from the Champagne region of France who became the observatory's "chief micrographist". In 1883, Miquel published a book on *Les organismes vivants de l'atmosphère*[315] (Living Organisms of the Atmosphere), in which he reviewed what was known about microorganisms, which he called *infinitely small*. He also discussed the conflicts surrounding Pasteur's discoveries on these subjects:

> "The majority of physicists regard M. Pasteur as a great benefactor to whom they are heartily grateful. Others, very few in number, have recently become slanderers of his work. I refer to a few noisy scientists from the other side of the Rhine, who, like the rest of us, have benefited from the immortal researches of Mr. Pasteur, and who, believing that they are now able to fly on their own wings, fill the scientific journals with unjust attacks on the man who is still, and will be for a long time to come, their master in the so delicate studies of the infinitely small. [...]

[315] Miquel, M.P., *Les organismes vivants de L'atmosphère*, Gauthier-Villars, Paris, 310 pp., 1883.

> The real progress in the science of the infinitely small, otherwise called microbes by M. Sédillot[316] dates from the day when M. Pasteur, overthrowing forever the obsolete theories of Liebig[317] on the decomposition of organic substances, taught us to detect in the dust of the air the germs of fermentations, to isolate them, to cultivate them, to follow them in their development and to measure their powerful action."

Since these early studies, air samples have been taken from many parts of the world and analyzed under a microscope. Bacteria, fungal spores, pollen, and algae have all been found. In the early twentieth century, small amounts of air were collected by aeronauts during their balloon ascents and analyzed in the laboratory. In the early 1930s, Charles Lindbergh took samples from the ice floes he flew over between the east coast of the United States and Denmark. In 1935, Captain Albert Stevens and Lieutenant Orvil Anderson, who participated in the Explorer II stratospheric flight (see Chapter 6), brought back to the Earth's surface several types of microorganisms (spores, bacteria, and fungi) from the layers between 12 and 20 km above sea level.

All of these studies show that the amount and type of microorganisms contained in airborne particles depend more on where they originate than where they are collected. These particles carry not only microorganisms, but also heavy metals, combustion products, pesticides, polyaromatic hydrocarbons, and other organic molecules. They move through the atmosphere on the wind before settling far from their point of origin. A significant amount of airborne sediment comes from arid and desert regions; the intensity of these sources is increased during droughts and by the development of agricultural activities. Microorganisms, which result from the decomposition of plant and animal matter, are particularly abundant in cities and buildings with large numbers of people. Mountain and ocean air, on the other hand, is relatively germ-free. The microbial content varies with ambient temperature and humidity and decreases with altitude. Air purifiers are sometimes installed in homes to reduce bioaerosol levels.

As early as the nineteenth century, an important public health question was raised: are pathogens attached to airborne particles capable of spreading disease and contaminating populations? Specifically, could the intercontinental transport of these particles explain the sporadic occurrence of outbreaks of infection in regions far removed from microbial foci? The question remained open, even though we now know that microbes adhering to sand grains can survive for several years, making desert dust a natural vehicle for the spread of microbial communities. Larger dust grains and those containing heavy metals are rapidly

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[316] In a paper presented to the Académie des Sciences in 1878, French surgeon Charles Sédillot (1804-1883) introduced the word "microbe" (from the Greek words μῑκκός (mikros, small) and βίος (bios, life)) to describe the microorganisms responsible for post-operative infections.

[317] In 1857, a controversy arose between Louis Pasteur and Justus von Liebig, the founder of agrochemistry, over the mechanisms leading to fermentation. Pasteur saw fermentation as a biological process in the absence of oxygen, while Liebig saw it as a chemical and mechanical process. Today, we know that fermentation transforms organic substances through the action of enzymes.

deposited on the Earth's surface, but finer particles, which remain suspended in the air for several months, are transported over long distances.

Airborne contamination of individuals is most likely to occur between people in close proximity, especially in confined spaces where viruses and bacteria are easily spread. This is the case for diseases such as the common cold, influenza, coronaviruses, pneumonia, tuberculosis, and certain gastrointestinal infections, as well as infectious diseases such as measles, chickenpox, and whooping cough. Finally, respiratory allergies are an immune response to the inhalation by sensitive individuals of certain airborne substances, such as those emitted by certain types of plants.

Particles in the Stratosphere

Major advances in the field of aerosols were made in the 1950s by German scientist Christian Junge (1912-2001). Junge came from the small town of Elmhorn near Hamburg in northern Germany. It was during his school years that the young student began to develop a real passion for aviation, which led him to take a keen interest in meteorology and weather forecasting. After graduating from high school, Junge decided to study at the University of Graz in Austria, where a renowned German professor taught atmospheric science: Alfred Lothar Wegener (1880-1930), a pioneer of polar research and author of the then-controversial hypothesis of continental drift. Unfortunately, Wegener was tragically killed during an expedition to Greenland. Junge abandoned his project and began his studies at the University of Hamburg, which he continued at the University of Frankfurt. After graduating, he joined the *Reichwetterdienst* (State Meteorological Service) in Hamburg but was soon forced by the National Socialist government to join the *Luftwaffe*, where he was initially put in charge of propaganda.

Junge's first assignment was to send small balloons with Nazi pamphlets to France. The young soldier then moved on to Italy, where he was in charge of weather forecasts for war pilots. Finally, still as a forecaster, he contributed to the activities of the German Expeditionary Corps in North Africa under Field Marshal Johannes Erwin Eugen Rommel (1891-1944). It was in the Sahara that Junge became familiar with sandstorms and was particularly interested in the injection and atmospheric transport of desert dust.

At the end of hostilities, Junge was taken prisoner of war by Allied troops and, after his release two years later, returned to the meteorological service in Hamburg, where he began a research project on fine particles in the atmosphere. In particular, he studied the increase in aerosol size under the influence of humidity. He also studied the conditions under which particles are activated to become condensation nuclei around which raindrops form.

By the early 1950s, however, the prospects for developing a lasting professional career in a war-ravaged Germany were slim. Junge accepted a position as a researcher at the US Air Force's *Cambridge Research Center* in Bedford, Massachusetts. The military wanted to determine whether its rocket launches were likely to alter the atmosphere. To address this question, Junge began measuring aerosols from hydrogen-filled balloons launched in South Dakota,

Florida, and India, among other places. The German researcher was the first to determine the chemical composition of atmospheric particles, observing the presence of sulfates $SO_4^=$, nitrates $NO3^=$, ammonium NH_4^+, and chlorine Cl^- in the air. Junge also showed that some of these aerosols consist of ammonium sulfate $(NH_4)_2SO_4$.

The Florida measurements also indicated that Saharan dust, which had interested Junge during his stay in North Africa ten years earlier, was being transported across the Atlantic and deposited on the American continent. This result was later confirmed by Texas A&M professor Robert Duce and University of Miami professor Joseph Prospero, who showed that these particles are a source of nutrients (especially iron) for the ocean and even for the Amazon rainforest.

The use of U2 military reconnaissance aircraft flying at very high altitudes enabled Junge to study the characteristics of aerosols at high altitudes. These measurements led to an important discovery: the presence in the stratosphere (at about 20 km) of a layer composed mainly of sulfates. The question was to identify where these fine particles were originating. Could they be of cosmic origin, as in the case of micrometeorite dust found at very high altitudes? Junge suspected that these particles were of terrestrial origin. He proposed that sulfur emitted from the ocean in the form of dimethyl sulfide (DMS) and carbonyl sulfide (COS) was oxidized in the atmosphere and converted to sulfates, which were transported to high altitudes. These are known as secondary aerosols. The layer of aerosols observed in the stratosphere is now known as the *Junge layer*.

By the early 1960s, the space race between the United States and the Soviet Union was in full swing. Now that it was known that satellites did not pose a

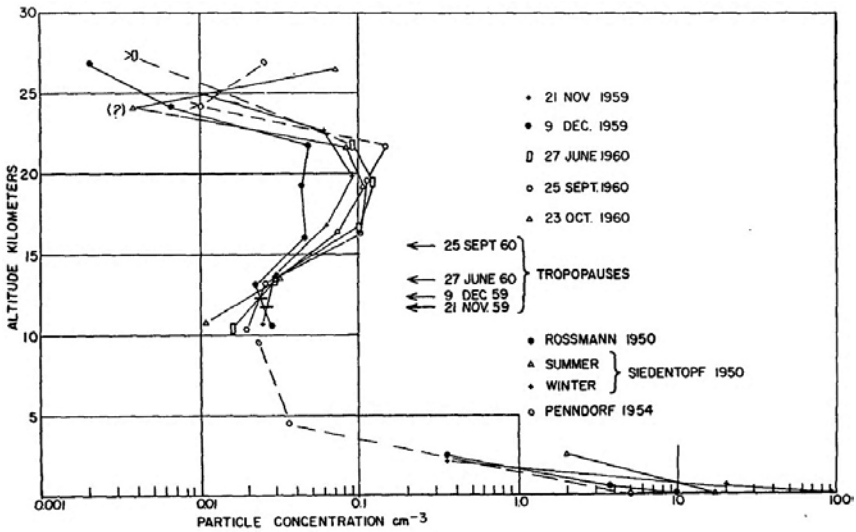


FIGURE 9.6: Vertical distribution of fine particle concentration in the atmosphere from ground level to 27 km altitude. The layer between 15 and 25 km altitude is known as the "Junge layer". Source: Duce, R.A., Dickerson, R.R., Galbally, I.E. *et al,* Christian Junge - a pioneer in global atmospheric, Chemistry, *J. Atmos. Chem.*, 79, 219-256, 2022.

significant threat to the upper atmosphere, the Air Force's research priorities changed. Junge returned to Germany, where he was appointed professor at the University of Mainz before becoming, in 1968, director at the Max Planck Institute for Chemistry (Otto Hahn Institute). It was during this professional transition that he began writing a book on *Air chemistry and radioactivity*. This work, which is still considered a reference today, illuminates the relationship between atmospheric chemistry and meteorology. Junge was the first to integrate the various elements known at the time into a unified doctrine that would make atmospheric chemistry a true discipline. Interestingly, it was a meteorologist who proved to be one of the best pioneers of a nascent discipline: atmospheric chemistry.

Together with his research team in Mainz, Junge continued his work on aerosols and expanded the scope of his interests. These included the entire chemical cycle of the Earth system and the question of planetary evolution.

Organic Aerosols

The work carried out by the scientific community in the 1960s and 1970s attributed the origin of most atmospheric particles to human activities, in particular the burning of fossil fuels. In 1960, however, a surprise occurred that led to a real debate within the scientific community in the years that followed: continental vegetation was thought to be a source of organic substances that served as precursors for the formation of fine particles. In other words, natural sources of organic aerosols were believed to often be higher than anthropogenic sources. Curiously, but not entirely inaccurately, this is what U.S. President Ronald Reagan said in 1981:

> "Trees cause more pollution than automobiles do."

On 10 September 1980, while he was a presidential candidate, he stated in an interview with the Sierra Magazine:

> "Approximately 80% of our air pollution stems from hydrocarbons released by vegetation, so let's not go overboard in setting and enforcing tough emission standards from man-made sources."

How do we know that trees are a natural source of atmospheric organic aerosols? The answer came in 1960 from Frits Warnolt Went (1903-1990), a scientist from Utrecht, Holland, who was working at the California Institute of Technology in Pasadena. This biologist, who later became director of the *Missouri Botanical Garden* in St. Louis, set out to find the origin of the "bluish haze" often seen when flying over rural areas, especially forests. After eliminating several possible causes, he concluded that these foggy episodes were most likely due to "the agglomeration or condensation of molecules already present in the air" in rural areas. In an article published in the journal *Nature*[318] in 1960,

[318] Went, F.W., Blue hazes in the atmosphere, *Nature, 187*, 641-643, 1960.

Went referred to laboratory work done by John Tyndall almost a century earlier, and noted that in those experiments.

> "When a beam of intense light was passed through a tube filled with air containing organic vapors, a delicate blue light was emitted by that part of the air through which the light had passed."



FIGURE 9.7: Christian Junge. With permission from Ruprecht Jaenicke.

He also pointed out that Arie Haagen-Smit, who studied the mechanisms of photochemical smog formation in Los Angeles, also found that a bluish cloud is formed when hydrocarbons from gasoline mix with ozone in low concentrations. He added that the hydrocarbons emitted by plants probably behave in a similar way to the organic matter in gasoline. A bluish haze often hangs over the Great Smoky Mountains, along the border of Tennessee and North Carolina in the southeastern United States. This national park, established in 1934, is part of the Appalachian Mountains. A bluish haze is also frequently observed over the Blue Mountains, a national park established in 1959 near Sydney, Australia.

For Went, it was likely that the bluish haze often observed over forested areas was related to physicochemical transformations initiated by the oxidation of hydrocarbons of biological origin. Organic molecules present in the atmosphere and produced by continental vegetation thus serve as precursors for the formation of these aerosols; among the most abundant species of biogenic origin are isoprene (emitted mainly by deciduous trees) and terpenes (emitted mainly by conifers). This discovery opened an important field of research on the transformation processes of volatile organic compounds present in the atmosphere. More importantly, it highlighted the influence of the biosphere on the chemical composition of the atmosphere.

Aerosols and Clouds

At the end of the nineteenth century, John Aitken (1839-1919) was the first to determine the atmospheric concentration of what he called dust particles. The career of this Scottish amateur meteorologist was extraordinary. After completing his secondary education in the small town of Falkirk (Stirlingshire), Aitken studied logic, chemistry, and mathematics at Glasgow University before going on to study civil and mechanical engineering. He became an engineer in 1857, working for a shipbuilding company, but health problems forced him to curtail and even abandon his engineering career. He retired in 1867 to his hometown of Falkirk, where the young "retired" bachelor lived with his two brothers.

He secured his financial independence with his parents' inheritance. He devoted himself to reading and gardening but became increasingly interested in natural phenomena, which led him to take courses. His professors of mechanics and thermodynamics at Glasgow University, William J. M. Rankine (1820-1872) and William Thompson (Lord Kelvin) (1824-1907), gave him new motivation and the desire to begin research into the processes that determine changes in the state of water. In his paper *On Dust, Fog and Clouds*, published in 1880, Aitken pointed out that the condensation of water vapor in the atmosphere takes place only around small solid nuclei, seeds so small that they are generally invisible. These nuclei consist of grains of dust suspended in the air; without these very fine particles, there would be no fog, no mist, no clouds, and probably no rain.

But was it really Aitken who made this fundamental discovery? In 1881, a Dutch astronomer from Groningen, Hendrik Jan Herman Groneman (1840-1908), who was interested in meteorite dust, denied this in a letter to the journal *Nature*:

> "In volume xxiii, p. 195 of Nature, I found an interesting summary of a paper read at the Royal Society of Edinburgh, on December 20, by Mr. John Aitken, showing that 'dust is the germ of which fogs and clouds are the developed phenomena'. My letter is in no way intended to diminish the value of the above article and experiment, but the same results have been obtained by Messrs. Coulier and Mascart (1875) in France[319]."

A debate was thus launched, fueled by other letters published in scientific journals. In France, Paul-Jean Coulier[320] (1824-1890) professor at the Val-de-Grâce military hospital in Paris, published a note on the subject in the *Journal de Pharmacie et de Chimie*[321] in 1875. In collaboration with the physicist and Collège de France professor Éleuthère Mascart (1837-1908), he showed, five years before Aitken's publication, that vapors condense on solid nuclei suspended in air. Upon learning of this discovery, Aitken responded elegantly in an article published in Nature:

> "I need not say that the information contained in M. H. J. H. Groneman's letter[322] in Nature, vol. xxiii. p. 337, was a most unexpected surprise. Nothing whatever seems to have been known in England about the results obtained by Messrs. Coulier and Mascart; and my astonishment was not diminished when I considered that their important investigation had borne no fruit, never having been practically applied by meteorologists or others."

All the work carried out at the end of the nineteenth century led to a significant advance in knowledge: we now know that cloud droplets are formed by the condensation of water vapor on fine particles. Subsequent studies show that

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[319] See *Naturforscher*, p. 400, 1875; *Journal de Pharmacie et de Chimie*, series 4, xxii, p. 165.

[320] Pharmacist, associate professor at the École de médecine et de pharmacie militaire du Val de Grâce in Paris (1853) and professor of applied chemistry and hygiene (1858).

[321] Coulier, P.J., Note sur une Nouvelle Propriété de l'Air. *Journal de Pharmacie et de Chimie, 22*, 165-173, 1875.

[322] Groneman, H.J.H., On dust, fogs, and clouds. *Nature*, *23*, 337, 1881. https://doi.org/10.1038/023337a0.

the activation process, which describes the initial growth of droplets in clouds, depends on the size and chemical composition of the aerosols. Their subsequent growth is governed by droplet collision accompanied by a coalescence process. At temperatures below about -35 °C, droplets can spontaneously freeze to form ice crystals. Ice particles can also form at higher temperatures when solid aerosol particles, such as mineral dust or soot particles, initiate droplet freezing or act directly as deposition nuclei.

Aitken, no doubt to preserve his fragile health and ensure that he was in an unpolluted atmosphere, wanted to measure the density of particles suspended in the air he breathed. Such a measurement should also provide a better understanding of the nature of the atmosphere. But how to measure the concentration of invisible particles? Aitken's answer was based on a physical principle that the Scottish engineer had discovered a few years earlier. Particles can be made visible by introducing them into a chamber supersaturated with water vapor[323]. Under these conditions, since each particle represents a nucleus on which water vapor condenses, they grow rapidly, become visible and can be counted. This made it possible to deduce the concentration of aerosols suspended in this volume of air, invisible at first. This device is sometimes called a *koniscope*.

Measurements taken with this instrument at various sites in Scotland revealed the enormous variability of atmospheric dust concentrations, ranging from 500 to 3 million particles per cubic centimeter. Aitkin then built a "pocket" version of his instrument, which he used to take measurements in several countries, allowing him to assess geographic differences and the effect of meteorological conditions. He visited several countries, climbed mountains in Switzerland, and took measurements at the top of the Eiffel Tower before the monument opened

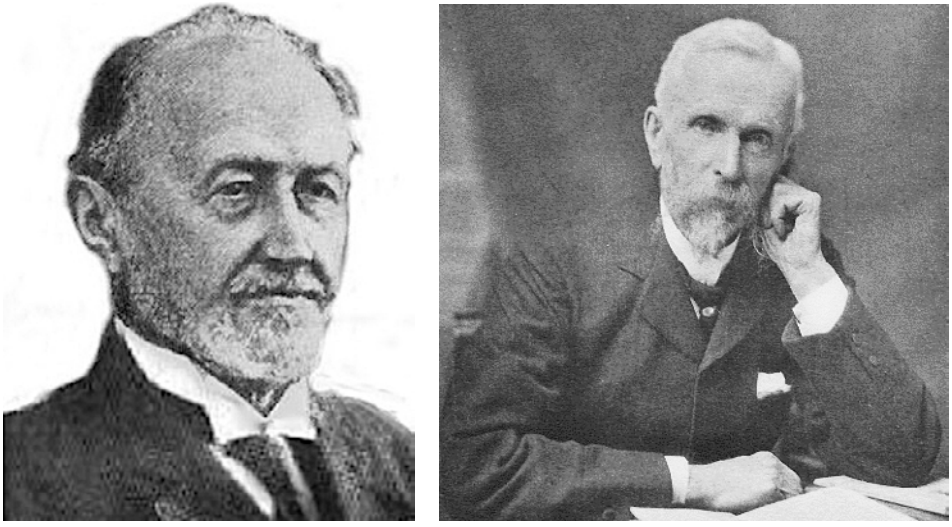


FIGURE 9.8: Left: Paul Jean Coulier. Right: John Aitken.

[323] That is, when the partial pressure of water vapor exceeds the saturation vapor pressure in the air.

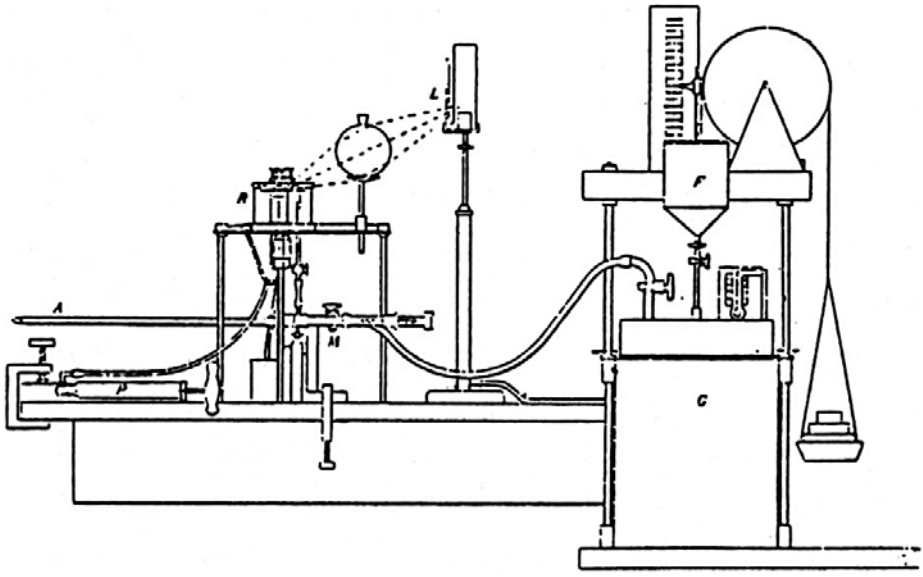


FIGURE 9.9: Illustration of the condensation nucleus counter developed by John Aitken in 1888-1889. Source: Podzimek, J., John Aitken's contribution to atmospheric and aerosol sciences - One hundred years of condensation nuclei counting. *Bulletin of the American Meteorological Society,* 70(12), 1989.

in 1889. He observed high levels of dust in the city of Paris, demonstrating once again that the air in large urban areas was polluted. To honor the work of this eminent scientist, the scientific community has given the name "Aitken particles" to atmospheric dust smaller than 0.1 micrometers.

Particles and Atmospheric Electricity

What is the origin of the 40,000 thunderstorms that occur every day around the world, with a total of 100 flashes per second? In ancient times, the lightning that accompanied these often violent phenomena was considered a manifestation of the unleashing of supernatural forces resulting from the wrath of the gods: Zeus for the Greeks, Jupiter for the Romans. During the Renaissance, more rational explanations were put forward, notably by René Descartes, who in 1737 explained the formation of thunderclouds by the meeting of hot and cold air masses. In the 18th century, lightning was associated with an electrical phenomenon comparable to the sparks and arcs produced by the newly invented electrostatic machines. The latter produced spectacular phenomena which were very fashionable at the time to entertain guests at glamorous salons.

To prove that lightning was indeed an electrical phenomenon, Benjamin Franklin conducted his famous experiment on June 15, 1752, using a kite unfurled beneath a thundercloud. The kite was connected by a hemp string to a *Leyden jar*, the forerunner of the capacitor developed in the Netherlands

in 1745 and capable of storing electrical charges. Despite Franklin's hopes of catching a bolt of lightning, the kite was not struck (which probably saved his life), but electrical charges had accumulated in the jar, which was placed on the ground.

Atmospheric electricity attracted the interest of several leading scientists. One of these was Laura Bassi (1711-1778), a physicist and mathematician who enjoyed a prodigious career in Bologna (Papal States, now Italy) while promoting the status of women in academia. Supported by Cardinal Prospero Lambertini (later Pope Benedict XIV), she became the first woman in the world to receive a doctorate in science at the age of 20 (1732). In the same year, she was appointed to the honorary position of Professor of Natural Philosophy at the University of Bologna. However, the university believed that women should have nothing more than a private life, so she was excluded from public teaching. For her work, however, she received an annual stipend of 500 lire, instead of the salary enjoyed by all other professors. After her marriage to the physician Giuseppe Veratti (1707-1793), she was allowed to give private lessons at home. She popularized Newton's work in Italy. Beginning in the 1760s, the couple conducted experimental research on electricity, with particular emphasis on atmospheric electricity. In 1776, two years before her death, Bassi finally became a professor of experimental physics, and her husband became her assistant.

In the nineteenth century, with the knowledge gained from laboratory work on electrical phenomena, several scientists studied the properties and effects of discharges produced by thunderstorms. At a time when Europe and North America were industrializing, it was important to protect infrastructures from lightning strikes, especially the power lines that were being built across these countries.

The idea that a real electrical circuit existed in the atmosphere between two conductive layers, the ionosphere, and the Earth's surface, gained ground in the twentieth century. In 1920, the Scottish physicist and meteorologist Charles T. R. Wilson (1869-1959), inventor of the cloud chamber and winner of the 1927 Nobel Prize in Physics, determined the structure of electrical charges in thunderclouds. He showed that during thunderstorms, these clouds deliver negative charges to the Earth's surface, making the ionosphere positively charged relative to the surface.

Subsequent work has shown that there is a downward electric field in the air, the value of which in the lower layers of the atmosphere is about 100-300 volts per meter. In regions where the weather is fair, the ions (electrically charged particles) produced by the action of cosmic rays on air molecules allow a downward electric current to be generated. This current tends to reduce the differences in electrical potential between the atmosphere and the ground. A neutralization of the charges with the disappearance of the electric field should therefore occur if there were no counteracting mechanisms generating these electrical phenomena. This mechanism results from the separation of electrical charges that occurs inside storm clouds due to microphysical and convective processes. Droplets with negative charges concentrate at the base of the cloud, while droplets with positive charges appear at the top of the cloud. An upward electric current is produced. The circuit is closed by currents in the conductive layers of the ionosphere and of the ground.

At the end of the twentieth century, other visible phenomena of electrical origin were observed in the upper atmosphere; their origin is still not fully understood. These include the "red ghosts" that appear above thunderclouds and reach mesospheric altitudes.

Aerosols and Climate

One of the fundamental questions in physical meteorology and climate science is the effect of aerosols on the penetration of solar radiation into the atmosphere. Some types of aerosols, such as soot, can absorb some of the sun's light, but other types of poorly absorbing particles can scatter the incoming light in all directions, including towards the interplanetary space, and thus reduce the amount of solar energy reaching the Earth's surface. This process, therefore, leads to a cooling of the planet and must be taken into account when estimating climate change.

It was the German physicist Gustav Mie (1868-1957) who theoretically studied the interaction of electromagnetic radiation with spherical particles. Mie studied mathematics and physics at the University of Rostock before moving to the University of Heidelberg, where he received his Ph.D. at the age of 22. From 1902, he taught at the University of Greifswald and from 1917 at the University of Halle. Between 1924 and 1935, he continued his research and teaching at the University of Freiburg in Breisgau in the state of Baden-Württemberg. It was at this institution that the man who became a member of the German Academy Leopoldina joined the "Freiburg Circle", a group opposed to the Nazi regime.

Mie derived a rigorous solution of Maxwell's equations for the special case of a plane electromagnetic wave interacting with a sphere. The results of his calculation, published in 1908, apply to particles whose diameter is of the same order of magnitude as the wavelength of the incident light. They differ from earlier results obtained by John William Strutt, third Baron Rayleigh (1842-1919), because the latter apply to molecules much smaller than the wavelength of the radiation.

Although the general theory of scattering is now known as "Mie scattering", it should be noted that other physicists and chemists have also successfully addressed this question. As early as 1863, the Prussian mathematician Rudolf Friedrich Alfred Clebsch (known as Alfred Clebsch) (1833-1872) published a dissertation on this very subject. In 1909, Peter Joseph Debye (1884-1966), winner of the 1936 Nobel Prize in Chemistry, also found a mathematical solution to this particular problem of electromagnetism.

Mie theory is important in determining the effect of the aerosol layer in the atmosphere on climate. It is used to calculate the direct effect of the scattering of sunlight by particles (aerosols and cloud water droplets), particularly those resulting from air pollution sources such as sulfates, nitrates, and organic aerosols. The absorption of sunlight by particles such as soot must also be considered. These processes, which reduce the amount of radiant energy entering the atmosphere, result in a cooling of the Earth's surface. At the same time, the absorption of the Earth's infrared radiation by particles, including soot or

ice crystals in high-altitude clouds (cirrus clouds) tends to warm the surface, amplifying the effect of greenhouse gases. Overall, according to mathematical models, the particles produced by human activities have the effect of cooling the Earth's surface and thus limiting the extent of warming caused by carbon dioxide, methane, and other greenhouse gases.

In 1990, Robert Jay Charlson (1936-2021), a specialist in the relationship between atmospheric gas chemistry and aerosol physics at the University of Washington, showed that anthropogenic sulfur particles in the Northern Hemisphere produce a radiative forcing comparable to that produced by greenhouse gases, but with the opposite sign. In his early work, he estimated this forcing to be about -1.6 watts per square meter (W/m^2), a value that should be compared to the forcing of about 2 W/m^2 produced by CO_2. Thus, Charlson believed that there is a quasi-compensation between two very different processes. Aerosols should therefore significantly limit the magnitude of climate change. Two scientists from the National Center for Atmospheric Research, Jeffrey T. Kiehl and Bruce P. Briegleb added an important nuance: the opposing effects of the two processes do not exactly cancel each other out at every point on Earth; they create temperature gradients that disrupt atmospheric dynamics. The most recent data suggest that the forcing from interactions between solar radiation and anthropogenic aerosols is only - 0.22 W m^{-2}, with an error bar ranging from - 0.47 to + 0.04 W m^{-2}. In any case, the value is much lower than Charlson's first estimate.

Interestingly, government efforts to improve public health by reducing the amount of anthropogenic aerosols in the atmosphere had the perverse effect of warming the planet. Thus, political leaders entered a veritable Faustian pact[324] as the journalist David Wallace-Wells has pointed out: that of improving air quality and thus human health, but at the expense of the climate, which they were also committed to preserving.

Other processes that could counteract the greenhouse effect were discovered. We know that aerosols act as "condensation nuclei" for the formation of the water droplets that make up clouds. The presence of anthropogenic aerosols in the atmosphere is therefore likely to modify the microphysical processes responsible for cloud formation, and thus have an indirect effect on climate.

Sean Twomey (1927-2012), was an Irish-born physicist with a degree from Galloway University who worked successively for the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia, the Weather Bureau, and the Naval Research Laboratory in the United States, before joining the University of Arizona, addressed this question. In 1977, this specialist in the microphysics of aerosols and clouds published a resounding article[325]. His work showed that an increase in the number of condensation nuclei resulting from air pollution should lead to an increase in the amount of solar energy reflected by clouds back to space, and thus to a cooling of the Earth's surface.

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[324] The expression is used by analogy with the pact made between Faust and the Devil in a German folk tale. In this tale, the Devil offers Faust a second life of pleasure in exchange for Faust's soul.

[325] Twomey, S., The influence of pollution on the shortwave albedo of clouds. *Journal of Atmospheric Science 34*, 1149-1152, 1977.

When particles of anthropogenic origin are added to those of natural origin in the atmosphere, the water that condenses into droplets is distributed over a greater number of condensation nuclei. Clouds are then formed from more numerous but smaller water droplets. As a result, they become brighter and reflect more solar radiation back into space. Cloud development, precipitation formation, and the radiative properties of clouds are therefore highly dependent on the properties of the atmospheric particles. Through the *Twomey effect*, air pollution significantly affects the radiative properties of clouds and thus the amount of solar energy stored by the Earth system.

Twomey also contributed to the development of mathematical methods for determining atmospheric physical quantities from observed values of optical parameters[326]. This work lays the theoretical foundations for remote sensing measurements from space or from the ground. Twomey proposed the use of an inversion method to determine, for example, the size distribution of fine particles from the optical thickness of the atmosphere measured as a function of wavelength. Such an inversion method can also be used to derive the vertical distribution of atmospheric ozone from a measurement of the spectral distribution of ultraviolet solar radiation that has passed through the atmosphere.

In addition to the Twomey effect, other indirect links between aerosols and climate were proposed. Bruce Albrecht of the University of Miami, for example, noted that an increased number of condensation nuclei slows the formation of large droplets that are likely to fall as rain. This, in turn, tends to increase the lifetime of clouds and, consequently, the amount of solar radiation reflected in space. The *Albrecht effect,* therefore, tends to cool the Earth's surface.

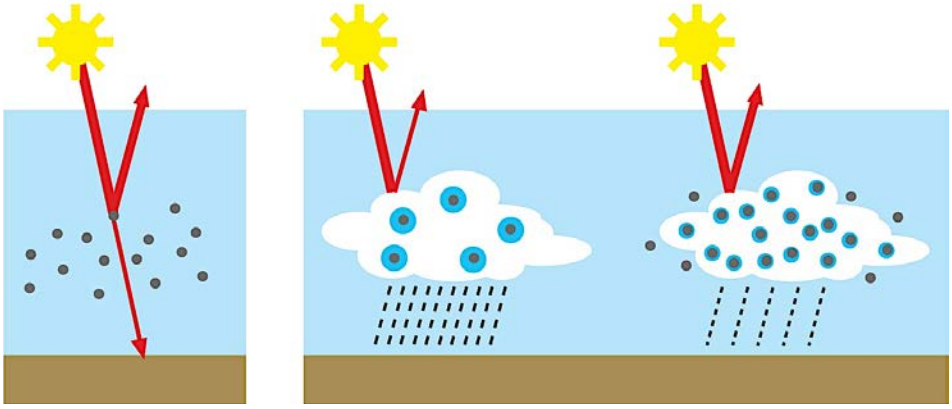


FIGURE 9.10: Scattering and reflection of incident sunlight (left) with the direct effect of aerosols from undisturbed clouds (center) and with the indirect effect of additional aerosols (Twomey effect), for example from air pollution (right).

[326] Twomey, S., *Introduction to the Mathematics of Inversion in Remote Sensing and Indirect Measurements*, Dover Publishing, 243 pp., 1996; and Twomey, S., *Introduction to the Mathematics of Inversion in Remote Sensing and Indirect Measurements*, Second Edition, Dover Publishing, 243 pp., 2014.

According to the most recent estimates, the indirect effect of aerosols on radiative forcing is on the order of - 0.84 W m^{-2}. However, this value is highly uncertain and lies in a "range" from - 1.45 to - 0.25 W m^{-2}. These effects, which involve cloud microphysics, are a major source of uncertainty in climate model projections.

10
The Human Footprint

Is it possible to find pure air in the Earth's atmosphere, that is, air whose chemical composition has not been altered by the presence of human beings? Are there preserved regions where the air is virtually identical to what it was hundreds of thousands of years ago? At first glance, the answer is no, since many anthropogenic gases can remain in the atmosphere long enough to be distributed to all regions of the world. This suggests that no region has been spared.

However, measurements of the chemical composition of the air taken by a team from the Laboratoire des Sciences du Climat et de l'Environnement in Gif-sur-Yvette near Paris and by Sonia Kreidenweis' group at Colorado State University in the USA confirm that there is probably one region that has been shielded from most of the effects of human activity[327]. French and American teams have discovered a relatively intact air mass overhanging the Southern Ocean around the Antarctic continent. It was the nature of the fine particles observed in the air of the planetary boundary layer that allowed the researchers to draw this conclusion. The only particles detected were bioaerosols, i.e., particles containing only bacteria, which are emitted locally by sea spray, to the exclusion of particles of continental origin. Measurements carried out by the French team on the island of Amsterdam in the southern Indian Ocean show a strong correlation between the content of carbonaceous particles in the atmosphere and chlorophyll activity, which changes with the seasons. The air masses surrounding Antarctica, which is highly isolated from the rest of the world, therefore appear to be relatively unaffected by human activity. However, atmospheric concentrations of long-lived gases, such as CO_2, measured in the southern regions are significantly higher than typical pre-industrial levels. Regions remote from human activity are therefore not completely immune to anthropogenic perturbations.

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[327] Sciare, J., Favez, O., Sarda-Estève, R., Oikonomou, K., Cachier, H., Kazan, V., Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source. *Journal of Geophysical Research*, *114*(D15302), 2009, https://doi.org/10.1029/2009JD011998; and Uetakea, J., Hilla, T.C.J., Moorea, K.A., DeMotta, P.J., Protatb, A., Kreidenweis, S.M., Airborne bacteria confirm the pristine nature of the Southern Ocean boundary layer. *Proceedings of the National Academy of Sciences of the United States of America, 117*(24), 13275-13282, 2020, https://doi.org/10.1073/pnas.200013411.

However, the situation that characterizes these air masses in the Southern Hemisphere is an exception to the situation in other parts of the world: in their attempt to dominate nature, human beings have indeed disturbed the planet to such an extent that the atmosphere and, more generally, the climate are threatened, sometimes irreparably.

Throughout history, societies have taken the view that humans are different from other living beings and have the right to exploit nature as they see fit. The Age of Enlightenment and the scientific and technological revolutions that followed demonstrated humanity's ability to harness natural resources for economic development and human well-being. But this has not come without a heavy price: the environment has been progressively degraded, first locally, then regionally, and globally. This degradation has been at the expense of the planet's inhabitants, their health, and in extreme cases, their very existence. Some of the most vulnerable regions could become uninhabitable.

In this chapter, we will look at a number of human endeavors over the course of the twentieth century that have disturbed the Earth's atmosphere and, in particular, the chemical composition of the air through combustion processes or the release of various pollutants into the atmosphere. We will expand in Chapter 11 our focus to include climate change, which is the direct result of increasing greenhouse gas emissions and the disruption caused by the presence of aerosols in the atmosphere.

Wildfires

How did humans gradually change the chemical composition of the atmosphere? Combustion is undoubtedly responsible for the first human disturbances of the air. Of course, large forest and savannah fires started by lightning have always existed and must be considered natural events; the oldest traces of fire found in sediments in China and Africa date back over a million years. Humans increasingly used these natural events to protect themselves from predators and to take advantage of the warmth and light that fire provided. They also lit fires in the caves in which they lived. But it was not until about 400,000 years ago that *Homo erectus* began to domesticate fire, using it for cooking, making tools, hunting, and developing agriculture.

It is believed that throughout history, fire has been a factor in the evolution of mankind, allowing us to improve our diet, protect ourselves from parasites, create new means of hunting, change our behavior, and make the earth more suitable for our lifestyle. But in the last 7,000 years, a new step has been taken. Fires were used in a "controlled" manner to clear forests, promote agriculture, and contribute to the war effort. Finally, with the Industrial Revolution of the 18th and 19th centuries, combustion became an industrial practice that enabled the processing of metals, the development of machinery, and the expansion of transportation, while releasing gases and particles into the atmosphere. The increased use of fossil fuels to meet growing energy needs, as well as the expected increase in forest fires due to global warming, represent

a major source of pollutants and particulate matter. This development, which characterizes the modern world, has led Stephen J. Pyne, professor emeritus at Arizona State University and a specialist in environmental history, to suggest that the geological period in which we live should be called the *"Pyrocene"* because we have entered a global regime dominated by combustion. He likes to point out that much of the Earth is indeed burning; coal and oil, farmland and forests, shrublands, and wetlands are often in flames. The proliferation of forest fires observed today and, increasingly, of large and destructive urban fires, sometimes over vast geographical areas, is probably a consequence of global warming and changes in ecosystems and water management. These dramatic events, caused either by lightning or by human negligence, are accompanied by plumes of smoke that spread over regions sometimes far from the burning areas. The use of fossil fuels in internal combustion engines in cars and trucks, in jet engines, and industrial and domestic applications is a source of greenhouse gases.

Combustion residues, released into the atmosphere as so-called *primary* pollutants, include carbon monoxide (CO) and carbon dioxide (CO_2), methane (CH_4), nitrogen oxides (NO and NO_2), sulfur dioxide (SO_2) and a range of organic compounds such as benzene (C_6H_6) and toluene ($C_6H_5CH_3$), polycyclic aromatic hydrocarbons, aldehydes, hydrogen cyanide (HCN), etc. Many of these reactive compounds are harmful to our health and are sources of so-called *secondary* pollutants such as ozone. Other compounds, including carbonic acid (H_2CO_3), nitric acid (HNO_3), and sulfuric acid (H_2SO_4), produced by the transformation of carbon, nitrogen, and sulfur oxides, contribute to the acidification of precipitation. In addition to these gaseous compounds, fires release particles in the air, particularly soot and organic aerosols. And, as Pyne pointed out, "everything we burn, we breathe". Combustion has become a major source of air pollution, highlighting the human footprint on the Earth's atmosphere.

Poison Gas as a Chemical Weapon

At the beginning of the twentieth century, an idea was gaining ground among government and military officials: why not repel would-be invaders or disperse aggressive demonstrators by dispersing poison gas that would make these undesirables back off? These gases could be lethal against enemies from outside the country; they would only be a deterrent when it came to repressing demonstrators who disturbed public order. Finally, and most cruelly, poison gas has been used to assassinate opponents or execute people in countries where the death penalty is in force. Making the air toxic, thus appears to be a new weapon of war, a tool of repression, or a means of delivering death.

In Germany, the renowned Prussian scientist Fritz Jakob Haber (1868-1934) developed a chemical weapon based on the use of chlorine (Cl_2) and phosgene ($COCl_2$). This weapon was used during World War I to end the trench warfare that paralyzed soldiers facing each other.

Haber's professional and personal career is both interesting and frightening. Considered one of the finest chemists Germany has ever known, Haber was born into a Jewish family in Breslau, Silesia (now Wroclaw, Poland). After completing his doctoral thesis at the Friedrich Wilhelm University (later Humboldt University) in Berlin, Haber, who had converted to Protestantism (Lutheran Church), presumably to escape the growing anti-Jewish sentiment in Europe, developed his professional activities at the University of Karlsruhe. It was there that he and his assistant, the English chemist Robert le Rossignol (1884-1976), developed a highly efficient process for synthesizing ammonia from atmospheric nitrogen (N_2) and hydrogen (H_2). This work won him the Nobel Prize in Chemistry in 1918. The engineer Carl Bosch (1874-1940), winner of the 1931 Nobel Prize in Chemistry, used this chemical mechanism to develop an industrial process that produced large quantities of nitrogen fertilizer. The "Haber-Bosch" process made it possible to feed a large part of the world's population at a time of rapid population growth, thus averting a global food shortage.

Harber supported the war led by Kaiser Wilhelm II (Kaiser Friedrich Wilhelm Albert Viktor of Prussia (1859-1941)). He was a supporter of the dominant ideology in his country: Pangermanism and Social Darwinism, which promoted natural selection at the expense of the less able. In October 1914, when German troops invaded Belgium, he signed the *Appeal to the Civilized World*, commonly known as the Manifesto of the 93. This document, written by ninety-three writers, artists, philosophers, historians, and scientists, highlights the fervor and commitment of German intellectuals to the war[328] during the Wilhelmian period[329]. Einstein refused to sign the document, finding it contrary to his universalist vision, and Max Planck, one of the signatories, later distanced himself from the text.

Haber, who was advising the Second Reich's War Ministry[330] on the production of explosives, wanted to use chlorine gas to drive the enemy out of the trenches. Combatants poisoned by these gases, with permanent health effects,

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[328] This document presents a series of denials designed to embellish Germany's image and win the support of German intellectuals. It reads: "It is not true that Germany is guilty of this war. Neither the German people, nor the German government, nor the German emperor wanted it. [...] It is not true that we criminally violated Belgium's neutrality. We have irrefutable proof that France and England were determined to violate this neutrality themselves, and that Belgium approved. [...] It is not true that the life or property of a single Belgian citizen was touched by our soldiers, without the hard necessity of a legitimate defense forcing them to do so. [...] It is not true that our troops brutally devastated Leuven. [...] The famous town hall, a historic monument, has been preserved. [...] It is not true that our way of waging war is contrary to the law of nations. Indiscipline and cruelty are not characteristics of our army [...] Believe that we will fight this battle to the end, precisely because we are a civilized people, a people to whom the traditions of a Goethe, a Beethoven and a Kant are as sacred as their home and their soil." The manifesto was signed by several Nobel Prize winners.

[329] The Wilhelmian period, named after Kaiser Wilhelm II (Wilhelm II, 1859-1941), refers to German history between 1890 and 1918 (Second Reich). It ends with the personification of Wilhelm II's power and culminates in the First World War.

[330] Germany's political regime between 1871 and 1918.

would be unable to continue fighting. However, the use of poison gas as a chemical weapon was banned by an international convention signed in The Hague in 1899 and ratified by the Reich in 1910. The first use of these chemical weapons took place on 22 April 1915 at Ypres, Belgium, when 150 tons of chlorine were dispersed in the air along the 6 km front line around the Yser River. Haber, recently promoted to captain in the Prussian Army, personally supervised the operation. Five thousand people, mostly French, Algerian, and British soldiers, died of asphyxiation, and more than fifteen thousand others were poisoned. This first use of a lethal gas provoked unanimous condemnation from many countries, including the United States. However, similar operations were repeated in other theaters, often using shells or bombs as delivery vehicles. After the war, Haber was indicted by the Allies as a war criminal, forcing him to seek temporary refuge in Switzerland. In 1920, he defended his actions by stating

"Gas weapons are nothing more cruel than flying pieces of iron."

His support for the Reich's military action was strongly opposed by his wife, Clara Immerwahr (1870-1915), the first woman to obtain a doctorate in chemistry from the University of Breslau. A staunch pacifist, she did not accept Haber's beliefs. On May 2, 1915, ten days after the first use of gas as a weapon of mass destruction and the day after a reception given by Haber to celebrate the success of the operation of Ypres, she killed herself in the garden of the couple's villa with her husband's service revolver. Haber left Berlin that morning for the Eastern Front, where he oversaw a similar military operation. A few years later, on October 25, 1917, Haber married Charlotte Nathan (1889-1979), but they divorced in December 1927.

Germany's defeat and humiliation following World War I was a profound disillusionment for Haber, who had lost his bearings and his values. He entered a period of depression that lasted throughout the 1920s. After his divorce in 1927, he said[331]:

> "I fight with ebbing strength against my four enemies: insomnia, the economic claims of my divorced wife, my lack of confidence in the future, and awareness of the grave mistakes I have committed."

Nevertheless, in 1918, after the end of hostilities, Haber became director of the Kaiser Wilhelm Institute for Chemistry and Electrochemistry in the Berlin suburb of Dahlem. At this institute, but without Haber's direct involvement, cyanide (CH_3OCCN) was developed for use as an insecticide and fumigant, known as *Zyklon-A*. Beginning in 1924, a new version of the product, this time called *Zyklon-B*, was stored in sealed cans for distribution by the Hamburg company Tesch and Satbenow, and used during World War II to murder thousands of Jews and other prisoners in the gas chambers of extermination camps.

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[331] Ich kämpfe mit schwindender Kraft gegen meine vier Feinde: Schlaflosigkeit, die wirtschaftlichen Ansprüche meiner geschiedenen Frau, mein mangelndes Vertrauen in die Zukunft und das Bewusstsein für die schweren Fehler, die ich begangen habe, See Lehrer, S., *Wannsee House and the Holocaust,* McFarland, Jefferson, NC, 2000.

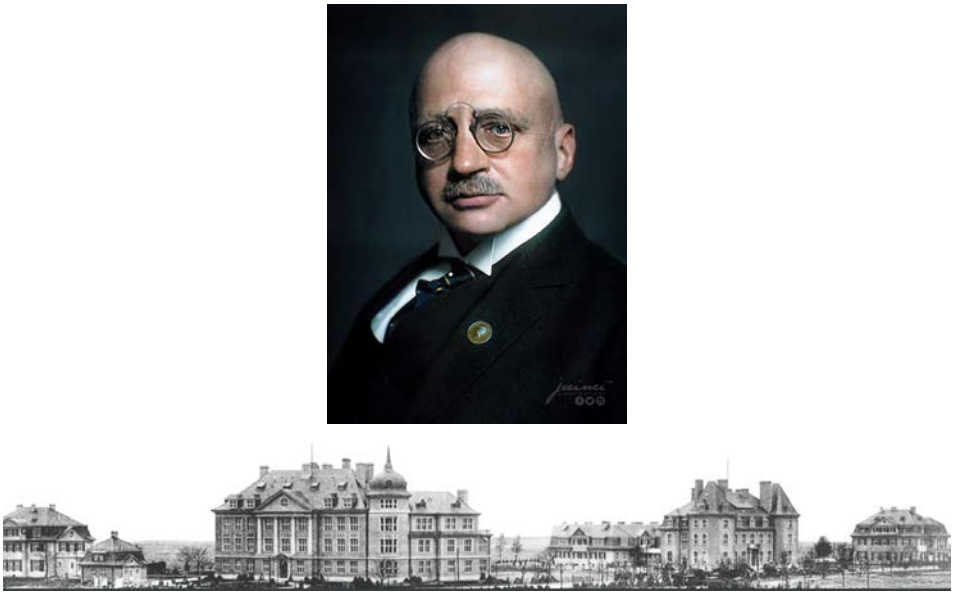


FIGURE 10.1: German chemist Fritz Haber (above) and two institutes of the Kaiser Wilhelm Society in Berlin-Dahlem: the Institute of Chemistry (left) and the Institute of Physical Chemistry and Electrochemistry (right) in 1912.

Beginning in April 1933, with Hitler's rise to power, Haber faced new difficulties. Civil servants of Jewish origin, including scientists and university professors, were dismissed by the Nazi government that had taken power three months earlier. Haber, a convert to Christianity, used this argument to delay his departure. He decided, however, to send a letter of resignation to Max Planck, President of the Kaiser Wilhelm Society, and Bernhard Rust (1883-1945), Minister of Education[332]. He left Germany in August 1933 and moved to England in November of that year to teach at Cambridge University. His contacts with the Russian-born biochemist Chaim Weizmann (1874-1952), the president of the Zionist Organization who would become Israel's first president in 1949, multiplied during the thirties. Weizmann told Haber of his intention to establish a research institute in Palestine and offered to help him realize his project. Although Haber's health was deteriorating rapidly, he decided to travel to Palestine to see the possibilities in that part of the world. During a stopover in Switzerland, he collapsed and died suddenly of a heart attack in his room at the Hotel Euler in Basel on January 29, 1934. The Research Institute was founded in April 1934 in Palestine, then under British Mandate. It was initially named the Daniel Sieff Research Institute in memory of a young

[332] Bernhard Rust, Minister of Science, Education and National Culture, in charge of immersing German youth in Nazi ideology. He had no hesitation in declaring to a group of scientists: "The problems of science are not the same for all men. The Negro or the Jew will see the same world in a different light to the German scientist". He committed suicide when Germany surrendered in May 1945.

researcher, the son of the founder of the British company Marks and Spencer (which financed the project), who died tragically at the age of 18. The research center, established in Rehovot, Israel, was renamed *the Weizmann Institute of Science* in November 1949 and was directed by Chaim Weizmann until his death on November 9, 1952. Today, it is one of the world's most prestigious research institutions. After World War II, the Dahlem Institute was taken over by the Max Planck Society as the Fritz Haber Institute.

In 1917, the Germans introduced a new toxic substance to the battlefield: "mustard gas," composed of the molecule dichlorodiethyl sulfide ($C_4H_8Cl_2S$), which had been synthesized in 1860 by the British chemist Frederick Guthrie (1833-1886), who had discovered its irritant properties. Affecting the respiratory tract, eyes, and skin, this mustard gas is also known as *yperite*, after the Flemish town of Ypres, where it was used extensively in the summer of 1917 to neutralize British troops stationed there. Phosgene ($COCl_3$), synthesized in 1812 by the chemist John Davy (1790-1868), was used by the French army from 1915. In all, nearly 1.3 million people, including 260,000 civilians, lost their lives following the use of these chemical weapons during World War I.

The use of chemical weapons continued in the following decades. During the Second Sino-Japanese War (1937-1945), phosgene was used by the Imperial Japanese Army against Chinese fighters. Mustard gas was used extensively in the Iran-Iraq War (1980-1988) and more recently in the Syrian Civil War. Sarin, a highly violent neurotoxic substance produced by the company IP-Farben of Wuppertal, Germany, in 1938 for use as a pesticide, blocks the transmission of nerve impulses in humans, causing rapid death by cardio-respiratory arrest. The product was not used by the Army of the Third Reich, but it was used for the first time on March 16, 1988, when Iraqi planes released this toxic gas over the Kurdish town of Halabja, killing over five thousand people. During the Vietnam War (1962-1971), the U.S. Army attempted to defoliate the forest and reduce the country's agricultural productivity by spreading powerful herbicides containing various chemicals. Between 1967 and 1969, more than 75 million gallons of these dangerous substances were sprayed over Vietnam, Laos, and Cambodia. The damage was considerable.

Various international initiatives have been taken to limit and even ban the use of chemical weapons. These include the 1889 Hague Convention prohibiting the use of poisons and poisoned weapons, the 1925 Geneva Protocol prohibiting the use of asphyxiating gases, and the 1993 Chemical Weapons Convention. These international agreements have often been violated.

The destruction of air quality also makes it possible to attack enemies from within a country. For example, less toxic gases are sometimes used by police to quell street demonstrations. As early as 1912, the prefect of police in Paris appointed a commission to determine how to dislodge criminals who had barricaded themselves in the city. The non-lethal gas chosen for this operation was ethyl bromoacetate ($CH_2BrCO_2C_2H_5$), known for its irritating and asphyxiating properties. In fact, this product was used by the French army in Alsace during World War I, but without much success. Today, tear gas is used by the police to quell riots and violent demonstrations. One of the gases ($C_{10}H_5ClN_2$), often

adopted, is characterized by the initials CS (named after the two Americans, Ben Corson and Roger Stoughton, who synthesized it in 1928).

Finally, execution of prisoners by asphyxiation or hypoxia (reduction of the amount of oxygen in the blood) was practiced by several totalitarian regimes, such as Nazi Germany, and by some American states that support the death penalty and are considering executing prisoners by having them breathe pure nitrogen.

Acid Precipitation

On October 24, 1967, the Swedish daily *Dagens Nyheter* published an article by Svante Odén (1924-1986) entitled "Nederbördens fösurning" (Acidification of Precipitation). Odén, a chemist specializing in soil science, was concerned about the increasing acidification of soil and water. Such a disruption would lead to significant degradation of the biosphere and wildlife, especially in lakes. The pH[333] of precipitation was reported to have fallen below 4.7 in most of Europe, and even below 4.0 in the Netherlands and northern Germany. According to Odén, the acidification of precipitation was mainly due to sulfur dioxide (SO_2) emissions from industry and was partly related to the production of electricity by burning fossil fuels (mainly coal). Pollutants transported to Sweden were coming mainly from industrial plants in Germany and the United Kingdom.



FIGURE 10.2: Svante Odén circa 1970 ©Ellis B. Cowling.

[333] *pH* or hydrogen potential: Quantitative value of a solution's acidity or alkalinity, measured on a scale from 0 to 14. Neutral solutions (such as pure water) have a *pH* of 7. Solutions with a *pH* below 7 are said to be acidic, those with a pH above 7 are said to be alkaline. *The pH* of raindrops is around 5.7 because they contain small quantities of carbonic acid, in particular bicarbonate ions. In the presence of nitric or sulfuric acid in polluted areas, the *pH of* raindrops can be much lower than in regions where the air is considered pure.

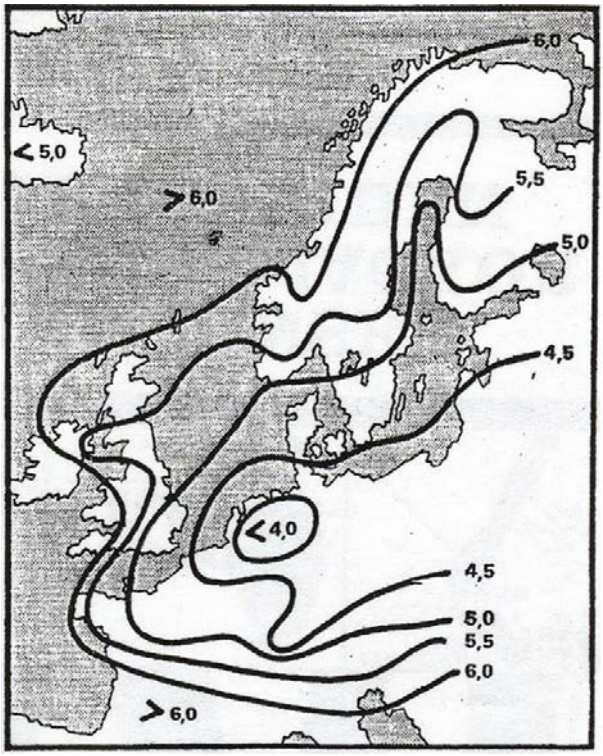


FIGURE 10.3: Precipitation *pH* distribution in Europe for the year 1962.
Source: Article published by Svante Odén in *Dagens Nyheter* on October 24, 1967.

The question of acidification by precipitation was not new. It had been raised as early as 1845 by Hippolyte Ducros in France and in 1872 by Robert Angus Smith in England. In the 1950s, the Canadian-American ecologist Eville Gorham (1925-2020), a specialist in biogeochemistry, described the influence of precipitation on lake acidification. But by the end of the "Golden Sixties", the problem had become acute, as it was the source of the observed degradation of the biosphere.

Odén's article caught the attention of the Swedish government, which immediately alerted the Organization for Economic Cooperation and Development (OECD) in Paris. Officials at this international institution were skeptical, believing that the pollutants were not transported over the long distances that separate the Nordic countries from the more southerly regions of Europe. Since the problem was local, the OECD said, it was beyond the scope of an international organization. Two years later, however, the OECD changed its mind. Now convinced that pollutants were indeed transported across borders, it launched a scientific study involving eleven European countries and concluded that air quality in all European countries was indeed affected by pollutant emissions in neighboring countries. The issue of acid rain thus took on an international dimension, and a European Monitoring and Evaluation Program (EMEP) was established in 1977 to address the challenge.

In the early 1970s, the Nordic countries developed research programs on soil acidification. However, they wanted to go further and involve more countries in the discussions, especially the Eastern Bloc countries that were also experiencing the harmful effects of acid deposition. Despite the tensions caused by the Cold War, talks were held, notably through Gro Harlem Brundtland (b. 1939), Norway's Minister of the Environment. In 1979, these talks led to the conclusion of a treaty under the auspices of the United Nations Economic Commission for Europe. The Convention on Long-Range Transboundary Air Pollution (CLRTAP) was signed by 51 countries. This first international agreement on air pollution was open not only to the countries of Western Europe, but also to Russia, the Eastern Bloc countries, and North America. The United States joined the Convention in 1981. A number of specific protocols were developed under the Convention, one of which focused on reducing emissions of heavy metals such as mercury, copper, and cadmium. Another protocol, known as the Gothenburg Protocol, aimed to reduce emissions of sulfur dioxide, nitrogen oxides and volatile organic compounds, thereby reducing acidification and ozone pollution.

Despite these initial political successes, the problem of acid rain continued to cause concern. In Germany, Bernhard Ulrich (1926-2015), director of the Institute of Soil Science in Göttingen, claimed in 1980 that forests were suffering severe damage from acid rain. He used measurements of sulfuric acid and heavy metals taken near his vacation home in Solling (a wooded hilly region in Lower Saxony, northwest of Göttingen) to show that air quality was deteriorating in areas far from industrial centers. Pollution was thus dispersed throughout Europe. The public response was enormous. The weekly magazine Der Spiegel ran the headline "The forest is dying," referring to the acid rain observed in Germany. At first, the industry tried to minimize its role and responsibility, but the issue became eminently political. The solutions to be found to save a forest so dear to Germans became an election issue in a highly emotional context. Newspapers showed photos of dying trees, especially in the "Black Triangle," a region of Central Europe bordering Poland, the German Democratic Republic, and Czechoslovakia. Protest turned into environmental activism: at a factory in Hamburg, for example, Greenpeace unfurled a giant banner on June 24, 1981, that read: "Only when the last tree has been felled, the last river poisoned, and the last fish caught, will you realize that you can't eat money." The problem of acid rain helped to develop the environmental movement. Governments responded by funding research in the field and taking the first steps to limit emissions, desulfurize industrial combustion, and introduce catalytic converters in cars.

In the early 1970s, Ellis B. Cowling (1932-2021), a distinguished professor at North Carolina State University, traveled to Sweden, where he met Svante Odén and discussed with him the possible effects of acid rain on the North American continent. Cowling invited Odén to the U.S. and Canada, where he gave a series of seminars. Both countries became aware of an environmental problem previously unknown in North America. One important discovery seemed to confirm the fears of American ecologists. Gene Elden Likens (b. 1935), a professor of limnology at the University of Dartmouth and a pioneer of scientific ecology who had visited Oden in Sweden in 1969, showed in 1972 that precipitation in the White Mountains of New Hampshire, a region far removed from the

industrial areas of the Midwest, was indeed highly acidic. His findings, published in *Science* in 1974, attracted media attention and put the issue on the North American environmental agenda. The First International Symposium on Acid Rain and the Forest Ecosystem, held at Ohio State University in 1975, marked the beginning of acid rain research programs in the United States. To support these efforts, the U.S. Congress passed the Acid Deposition Act in 1980, establishing the National Atmospheric Deposition Program (NAPAP) to implement a scientific approach to reducing acid deposition on soils. As in Europe, the problem quickly took a political turn: industry, particularly the power sector, which felt that the source of the problem was not clearly understood, strongly opposed any action to limit emissions of sulfur and nitrogen oxides. For industry, such measures were premature and would inevitably lead to higher electricity prices. This view was shared by scientists such as the Austrian-born American physicist Siegfried (Fred) Singer (1924-2020), who tried to convince Congress to oppose any restrictive measures. As for President Ronald Reagan (1911-2004), he initially refused to attribute acid rain to industrial sources but changed his mind in 1988 after a visit to Canada, where he saw the damage to the forest. As a result, he honored the agreements made at the instigation of then Canadian Prime Minister Pierre Trudeau. In 1990, NAPAP's work led to several amendments to the Clean Air Act and cooperative agreements between the United States and Canada. The goal of the 1990 Act was to reduce U.S. sulfur dioxide emissions by 50 percent by 2010. This goal has been met: U.S. SO_2 emissions, which were 17.3 million tons in 1980, were reduced to 7.6 million tons in 2008. Very significant reductions in SO_2 emissions have also been observed in Europe.

Despite the progress made in Europe and North America in the last three decades of the twentieth century, excess acidity in precipitation remains a worrying problem today, particularly in China and Russia. Further, the scope of research had to be broadened. On the one hand, we need to better understand the causes of forest dieback, which appear to be more complex than initially thought. Second, we need to look at the problem of air pollution in a broader context, including issues related to the effects of pollutants on health. Finally, we need to consider the influence of climate change. The geographical scope of these studies also needs to be broadened, since air pollution occurs throughout the Northern Hemisphere and even on a global scale. For this reason, the Task Force on Hemispheric Transport of Air Pollution (HTAP) was established in 2004 under the 1979 CLRTAP Convention to study the intercontinental transport of air pollutants.

The great scientific and political adventure of acid deposition began with Svante Odén's article in 1967. But what has become of this pioneer who alerted public opinion to this important problem for the future of the planet? In July 1986, while testing a secret instrument designed to detect the presence of submarines, he disappeared in the Baltic Sea near Roslagen in the Stockholm archipelago. His motorboat was found intact, but his body and the instruments, apparently of interest to American and Soviet intelligence, were never recovered. In any case, the problem raised by Odén mobilized the scientific community in an extraordinary way and led to the successful solution of a problem of great importance to society.

Supersonic Aviation and the Ozone Layer

In the "golden sixties", society was confident and optimistic: technological development was believed to enable rapid progress and to master nature. Civil aeronautics engineers believed that the construction of a new airliner flying at Mach 2 or 3 would make it possible to meet many challenges, such as transporting passengers from Paris to New York in less than four hours. France and Great Britain therefore decided to develop an aircraft called *Concorde*, which would become the flagship of European aviation. At the same time, the Soviets were building the *Tupolev 144*, whose architecture was strikingly similar to that of the Franco-British plane. As for the Americans, who were a little behind schedule with the design of their "Supersonic Transport" (SST), they intended to deploy a fleet of 500 aircraft that would fly at a speed of Mach 3 and at an altitude of 20 kilometers. The main project was entrusted to the Boeing company, which drew up plans for the construction of a revolutionary aircraft: the *Boeing 2707*.



FIGURE 10.4: Drawing of the Boeing 2707, the American supersonic aircraft.

Meanwhile, in his office at the University of Arizona in Tucson, James McDonald, a member of the American Academy of Sciences and a firm believer in the existence of unidentified flying objects (UFOs), believed that this project would endanger the ozone layer that protects living beings from solar ultraviolet rays. He asserted with great conviction that the water vapor emitted by aircraft engines into the stratosphere would inevitably destroy part of the ozone layer and thus cause a significant increase in the number of skin cancers among the population. His comments were echoed by environmental movements, which launched an information campaign against the construction of the SST.



FIGURE 10.5: James McDonald gives an interview to KSTP-5 television on May 26, 1969. Source: The University of Arizona.

In July 1970, the problem of air pollution from supersonic aircraft was addressed at a seminar organized by MIT at Williams College in Williamstown, Massachusetts, under the title *"Study of Critical Environmental Problems*" (SCEP). The report of this study, conducted in preparation for the Stockholm Conference on the Environment in July 1972, was not alarmist:

> "No problems should arise from the introduction of carbon dioxide [by supersonic aircraft]. And ozone reduction due to interaction with water vapor or other exhaust gases should be insignificant [...] Carbon monoxide and nitrogen oxides could also play a role in stratospheric photochemistry, but these contaminants are much less important than added water and can be neglected."

Despite these optimistic words, President Nixon's administration, which was very much in favor of the project for civil aviation, was concerned. Public opinion had to be reassured by a clear statement from atmospheric specialists. A task force was established by the U.S. Department of Transportation. On March 18-19, 1971, a task force chaired by Joseph O. Hirschfelder (1911-1990), a renowned physicist and professor at the University of Wisconsin known for his involvement in the Manhattan Project during World War II, met at the National Center for Atmospheric Research (NCAR) in Boulder to study the possible effects of the aircraft on the chemical composition of the stratosphere.

The debate was heated. The meteorologists in the room pointed out that aircraft effluents dissipate quickly in the atmosphere and therefore pose little danger. The chemists were divided. A mathematical model developed by Jae Park, a student of Professor Julius London (1917-2009), at the University of Colorado took into account a number of chemical reactions specific to the stratosphere. It showed that only 1.8% of the ozone layer would be destroyed by water vapor emissions if 500 supersonic aircraft flew overhead for eight hours a day. Another chemist, Frederick Kaufmann of the University of Pennsylvania, raised objections: the model's results were inaccurate because certain chemical processes were not taken into account, and in several cases, the reaction rates assumed in the models did not match laboratory measurements.

At this point, Harold Johnston (1920-2012), a specialist in chemical kinetics at UC Berkeley, took the floor to argue that it was not so much the release of water vapor that was to be feared as the emission of nitrogen oxides; these chemical species would be produced in large quantities in the combustion chamber of aircraft engines and would react rapidly with ozone. Johnston added that the chemistry of these nitrogen oxides was not fully accounted for in Park's model. The audience, somewhat surprised by these unexpected remarks, was skeptical. At the end of the first day, the general feeling was that the impact of a future SST on the ozone layer would be so small that it could probably be ignored.

Johnston disagreed. He retired to his hotel room that evening and spent most of the night drafting a 16-page handwritten note explaining how nitrogen oxides from aircraft would attack ozone in the stratosphere. The next morning, he presented his document and asked his colleagues to vote on a "motion" to recognize the overwhelming role of nitrogen oxides. The motion was defeated for lack of a majority.

Johnston was not distraught. He immediately wrote an article for the journal *Science* claiming that the nitrogen oxides emitted by a future fleet of 500 SSTs could cause ozone depletion of up to 50 percent. He wrote:

> "Although a great deal of attention has been given to the role of water vapor from supersonic transport (SST) exhaust in the stratosphere, oxides of nitrogen from SST exhaust pose a much greater threat to the ozone shield than does an increase in water."

At the time of the paper's submission, the Berkeley professor was unaware of Paul Crutzen's work in Europe and therefore made no reference to it. A few months earlier, Crutzen had shown that the main process of stratospheric ozone destruction results from a catalytic cycle involving nitrogen oxides. Johnston's article, which in its final version referred to Crutzen's work, prompted the U.S. Congress in 1971 to establish a special research program, the *Climatic Impact Assessment Program* (CIAP), to study the potential effects of the proposed supersonic aircraft. The mission statement was:

> "In order to determine regulatory constraints on flight in the stratosphere such that no adverse environmental effects result, CIAP will assess ... the impact on man, plants, and animals of climatic changes which may occur from the operation of a worldwide stratospheric fleet as projected to 1990."

Similar, less ambitious programs, called COVOS (*Comité pour l'étude des conséquences des vols stratosphériques*) in France and COMESA (*Committee on Meteorological Effects of Stratospheric Aircraft*) in the United Kingdom, were set up in the two countries that developed Concorde.

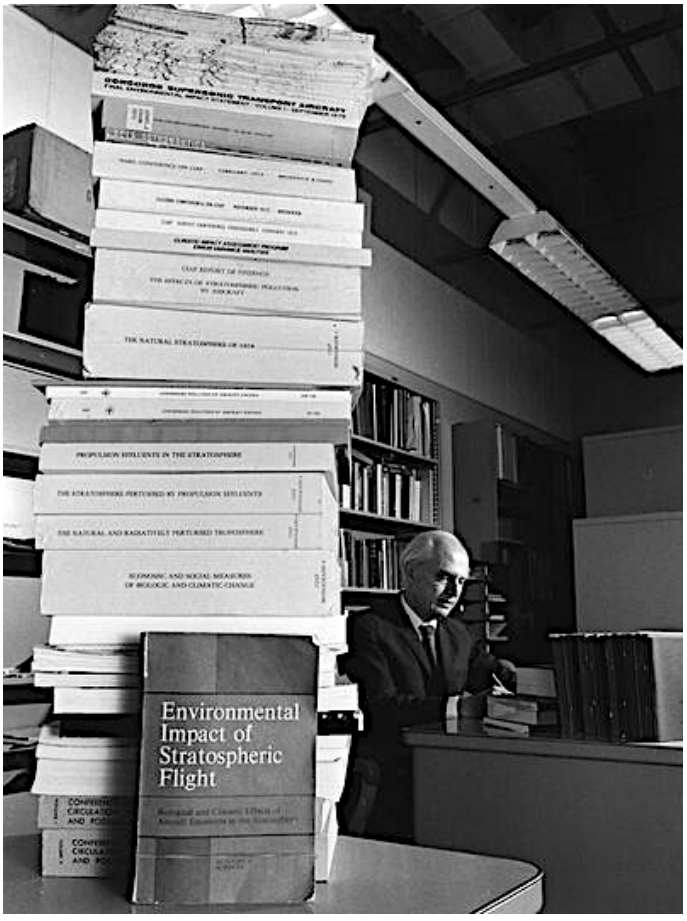


FIGURE 10.6: Harold Johnston in his office at the University of California, Berkeley, next to a stack of reports on the effects of supersonic aircraft on the ozone layer. DR.

Several hundred researchers in the United States and elsewhere in the world were mobilized to study the processes specific to the stratosphere, a layer of the atmosphere still poorly understood and often referred to by specialists as the *ignorosphere*. Measurement campaigns were organized, often using giant helium-filled balloons carrying sophisticated instruments to altitudes of up to 40 km. The scientists detected the presence of various chemical species and measured their concentration as a function of altitude. In the laboratory, chemical kinetics specialists measured the speed of an impressive array of reactions that take place at altitude. Modelers simulated the dispersion of jet engine exhaust and determined its impact on the stratospheric ozone layer.

The conclusions of the CIAP, COVOS, and COMESA reports were reassuring. This was especially true of the American report, which stated that a fleet of 500 supersonic aircraft would deplete the ozone layer by only a few percent and would only slightly increase the intensity of solar ultraviolet radiation reaching the Earth's surface. The American government seemed to have won the day. However, not all researchers involved in the CIAP program shared the optimism of the federal authorities, and many believed that the conclusions presented reflected the views of the Department of Transportation rather than those of the scientific community. For example, in an article published in the journal *Science*, Thomas Michael Donahue (1921-2004), chairman of the Department of Atmospheric and Oceanic Sciences at the University of Michigan and a member of the U.S. Academy of Sciences, accused Alan J. Grobecker (1915-1998), the director of CIAP, of denying the scientific results of the study he directed and of discrediting personalities such as McDonald, Crutzen and Johnston, who had sounded the alarm and were now accused of having given advice detrimental to the country. As for the report prepared by the members of COVOS, it was never published, since the French government considered that conducting a study on the effects of Concorde was tantamount to admitting that there was a potential problem.

Apart from the environmental aspects, economic studies showed that the American supersonic aircraft was unlikely to be profitable and could ultimately be a commercial failure. It was essentially this last argument that, on March 18, 1971, led the House of Representatives to vote to abandon the project (215 votes to 204). The decision was confirmed on March 25 by a vote in the Senate (51 to 46).

Only 16 Concorde were built in Europe, and commercial flights, which began in 1976, were finally discontinued in 2003, especially after the accident at Roissy in France in July 2000. As for the Tupolev 144, its operation as a passenger aircraft was short-lived due to two serious accidents, one at the Paris Air Show in 1973 and the other at Yegorievsk in 1978. As for the model of the American prototype, it has been exhibited in several museums.

A Hole in the Ozone Layer

In the 1980s, the problem of stratospheric ozone took on a new dimension. It became apparent that the protective layer formed by this gas, which absorbs ultraviolet solar radiation, could be significantly altered by a number of industrial products emitted into the atmosphere. An article published on May 16, 1983, in the journal *Nature* by Joseph Charles (Joe) Farman (1930-2013) and his collaborators Brian G. Gardiner and Jonathan D. Shanklin sounded the alarm: for several years, a significant decrease in the amount of ozone had been observed over the Antarctic continent during the austral spring (September and October). A few weeks later, the news was reported in the *New York Times* by the journalist Walter Sullivan (1918-1996), who popularized the term "hole in the ozone layer" and turned it into a metaphor widely used by both the environmental movement and scientists themselves.

Farman (1930-2013) was a Cambridge University graduate. After working for the aeronautical company de Haviland, he joined the *Falkland Island Dependency Survey* (now the *British Antarctic Survey*) in 1956 and devoted the rest of his career to scientific work in Antarctica. In particular, he oversaw ozone measurements at the British polar station at Halley Bay. Farman used a spectrometer identical to that developed by Gordon Dobson at Oxford in the 1920s. Measurements at Halley Bay began in 1958 during the International Geophysical Year, and by the early 1980s, the routine work of continuously monitoring the atmosphere in this remote part of the world had become tedious. In the early 1980s, however, Farman's attention was drawn to an unexpected phenomenon: the ozone layer seemed to get thinner and thinner each year during the austral spring (October). The ozone column fell from 300 Dobson in the early 1970s to 200 Dobson in 1984. A decrease of more than 30 percent in 10 years! Was this a decrease related to a change in stratospheric conditions, or was it simply the manifestation of a drift affecting the instrument used by Farman?

How to solve such a mystery? On the one hand, measurements taken in 1981 and 1982 at the Syowa polar station by Shigeru Chubachi (b. 1948), a member of the Japanese Meteorological Agency, showed that ozone levels were also extremely low at this station. On the other hand, data collected in the southern hemisphere outside the Antarctic region had to be taken into account; these measurements did not show this ozone deficit. Thus, the phenomenon identified by Farman and Chubachi seemed to be limited to the region inside the huge vortex[334] that surrounds the southern continent in the stratosphere. This vortex acts as a barrier, preventing air from other parts of the world from entering the Antarctic continent, and stratospheric temperatures are particularly low in this part of the world (around -80 °C).

Ozone measurements from space would have been particularly useful at this time to characterize the geographic extent of this ozone anomaly. NASA, with its satellites constantly measuring ozone, could have announced the appearance of this disturbance in the Antarctic region. As early as October 1983, specialists from the U.S. space agency had observed this phenomenon, which no model had predicted, and therefore feared that it was due to an instrumental problem. NASA held back until it was convinced that the phenomenon was real. It wasn't until August 1985, at an international conference in Prague, that NASA's Pawan Kumar (PK) Bhartia presented the first satellite image that clearly showed the existence of an ozone hole over the South Pole.

A second important piece of information came from ozone soundings taken above the American Amundsen-Scott station at the South Pole. Measurements taken by small balloon probes showed that during September and October, ozone virtually disappeared between altitudes of 16 and 26 kilometers. The ozone destruction that occurred during the austral spring was therefore limited

[334] In the southern hemisphere, the "polar vortex" surrounds the low-pressure area over Antarctica, with air flowing in a clockwise direction. The "polar vortex" in the Northern Hemisphere surrounds the low-pressure area over the Arctic with air flowing counterclockwise.

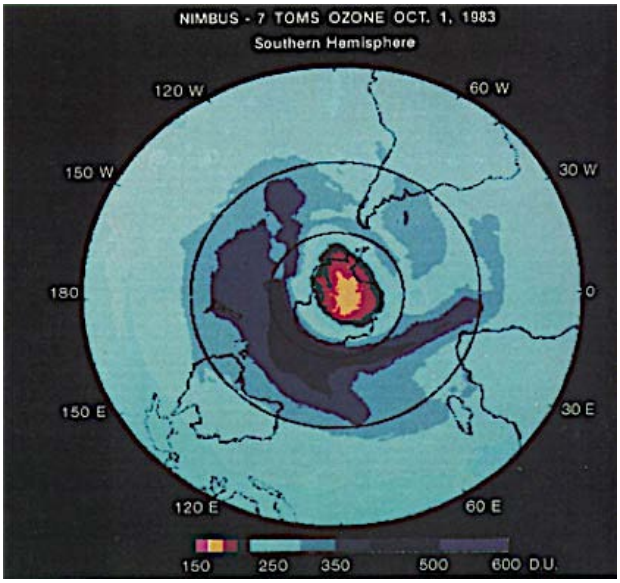


FIGURE 10.7: Original image of the ozone hole on October 1, 1983. Source: Bhartia, P.K., Heath, D.F., Fleig, A.F., Paper presented at the Symposium on Dynamics and Remote Sensing of the Middle Atmosphere, 5th Scientific Assembly, International Association of Geomagnetism and Aeronomy, Prague, 1985.

to a 10 km thick layer in the lower stratosphere over Antarctica. What was this particular destruction process that occurred only in a specific region of the atmosphere between two well-defined altitudes?

Several hypotheses were proposed. Some members of the meteorological community suggested a reversal of the atmospheric circulation, no doubt temporary, resulting in the injection of ozone-depleted tropospheric air into the lower stratosphere. This explanation was not accepted, however, because the proposed effect would have affected other chemical species, which were not observed. For some other scientists, the intensity of the flux of energetic particles intercepted by the Earth increased abnormally during periods of high solar activity, producing abnormally high amounts of nitrogen oxide in the upper layers of the atmosphere and, according to Crutzen's theory, causing significant destruction of stratospheric ozone. Again, the explanation was implausible because it did not explain why ozone is destroyed only below 26 km altitude.

A third hypothesis had to be considered. Farman, in his *Nature* article, had already mentioned the possible role of chlorine atoms released into the atmosphere by the photochemical destruction of chemical substances produced by industry under the influence of solar ultraviolet radiation. These were molecules containing chlorine and fluorine, known as *chlorofluorocarbons*[335] (CFCs).

[335] The two main molecules produced by the industry at the time were CFC-11 and CFC-12, whose chemical formulas are $CFCl_3$ and $CF_2\ Cl_2$ respectively.

Frédérick Swarts (1866-1940), a professor at the University of Ghent in Belgium and a member of that country's Royal Academy, was the first to synthesize a chlorofluorocarbon molecule at the end of the 19th century. Substances in this chemical family soon became attractive for many commercial applications because they were stable, nontoxic, noncorrosive, and nonflammable. For example, in 1928, Thomas J. Migley (1889-1944), best known for proposing the use of lead as an additive in automobile gasoline, proposed the use of CFCs as a refrigerant to replace the ammonia that had been used in refrigerators and was often associated with serious problems. This enthusiastic and optimistic industrialist advocated the use of the new chemical substance, which he believed to be harmless, in a variety of industrial applications. At the American Chemical Society meeting in April 1930, he went so far as to ingest CFC and exhale it over the flame of a candle to prove that the substance was nonflammable and nontoxic. In 1934, this product was taken over by the American company *Frigidaire* under the trade name *Freons*. Later, CFCs were used in air conditioning systems and as propellants in most aerosol cans. The idea behind these aerosol cans was developed in Oslo in 1926 by Erik Rotheim (1898-1938), a graduate of the Swiss Federal Institute of Technology (ETHZ) and the Karlsruhe Institute of Technology (KIT). It was only after the untimely death of this Norwegian engineer at the age of 38 that aerosol cans were popularized and used for insecticides (1942), hairspray (1948), shaving foam (1949), and paint products (1949). Other products containing bromine atoms, marketed as *halons*, were used in fire extinguishers. Hailed by his peers as an engineer who had made science truly liberating and whose wealth would recognize the lasting value of his inventions, Migley suffered a paralyzing attack of polio in 1940. He continued to work from his bed, however, and invented a system that allowed him to stand and move. It was a cord from this system that strangled him in 1944, killing him at the age of 55. At the time, no one understood the dangers of CFCs to the ozone layer.

Given the long residence time of these chemicals in the atmosphere (several decades), it's not surprising that when CFC molecules are released into the air, they disperse throughout the Earth's regions and reach high altitudes before being gradually destroyed. It was *James Lovelock* (1919-2022) who first detected the presence of CFCs in the atmosphere in April 1971. The measurements were made using a gas chromatograph aboard the research vessel *Shackleton*, which was sailing in the Atlantic Ocean between England and Antarctica.

In 1974, two researchers at the University of California at Irvine, Mario Molina and F. Sherwood (Sherry) Rowland, who had learned of Lovelock's measurements, calculated that CFCs were the main source of chlorine in the stratosphere. Rowland was a tall, imposing figure who presented his scientific arguments clearly and forcefully. He studied at the University of Chicago, where he benefited from the teaching of such illustrious masters as Enrico Fermi (1901-1954), the creator of the first nuclear reactor and one of the architects of the atomic bomb, and Harold Urey (1893-1981), a specialist in isotope separation who discovered deuterium. Both were Nobel Prize winners. As for Mario Molina, a Mexican post-doc who earned his Ph.D. at the University of California at Berkeley after attending universities in Mexico and Germany, he was hired by

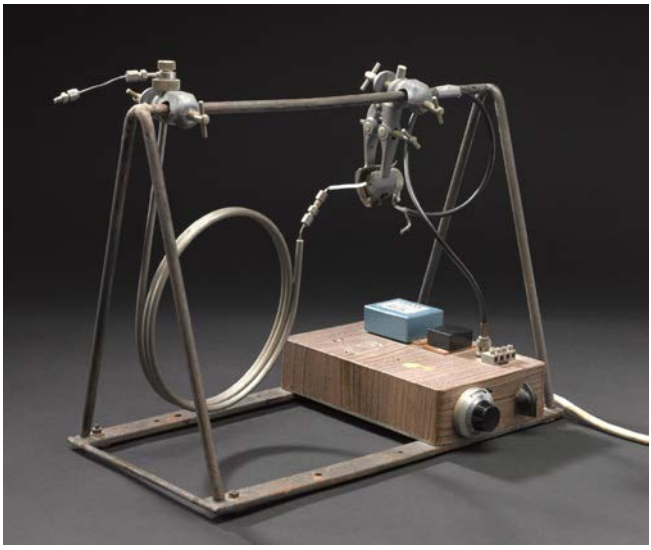


FIGURE 10.8: The gas chromatograph used by James Lovelock to measure the chemical composition of the atmosphere aboard the RSS Shackleton in 1971. This instrument was used to detect the presence of chlorofluorocarbons (CFCs) in the atmosphere. Air is injected (top left). The gases in the air sample are then separated by molecular weight in the loop shown in the center of the figure. The compounds are identified by the electron capture detector and the results are recorded in the device at the bottom of the instrument (right). © The Board of Trustees of the Science Museum.

Rowland at the University of California at Irvine. In a stunning article published in *Nature*, the two researchers showed that the photochemical destruction of CFCs provides a source of chlorine atoms capable of effectively destroying the ozone molecule through a catalytic mechanism discovered the same year by Richard Stolarski and Ralph Cicerone (see Chapter 8). Mathematical models that took these processes into account showed that the chlorine in CFCs was likely to reduce the thickness of the ozone layer by a few percent, but they did not predict the appearance of an ozone hole over Antarctica.

Ozone depletion is determined by the atmospheric content of a highly reactive radical, chlorine oxide ClO, which is produced by the reaction between the chlorine atom (released from the CFC destruction) and ozone. The reason why the thickness of the ozone layer has not been rapidly and significantly reduced by the CFCs dispersed in the atmosphere is that ClO is largely converted into inorganic reservoirs of chlorine (e.g., HCl, $ClONO_2$), which are not very reactive and therefore not capable of destroying ozone. This chemical mechanism has made it possible to limit the destruction of the ozone layer and thus to protect life from the consequences of the industrial production of CFCs.

But how to explain the sudden destruction of ozone in the Antarctic region? NOAA scientist Susan Solomon had a brilliant idea. She studied satellite data showing that clouds of ice particles form in the very cold air masses trapped inside the southern hemisphere's polar vortex during the southern winter and spring. Such stratospheric clouds were first observed in the polar regions of the

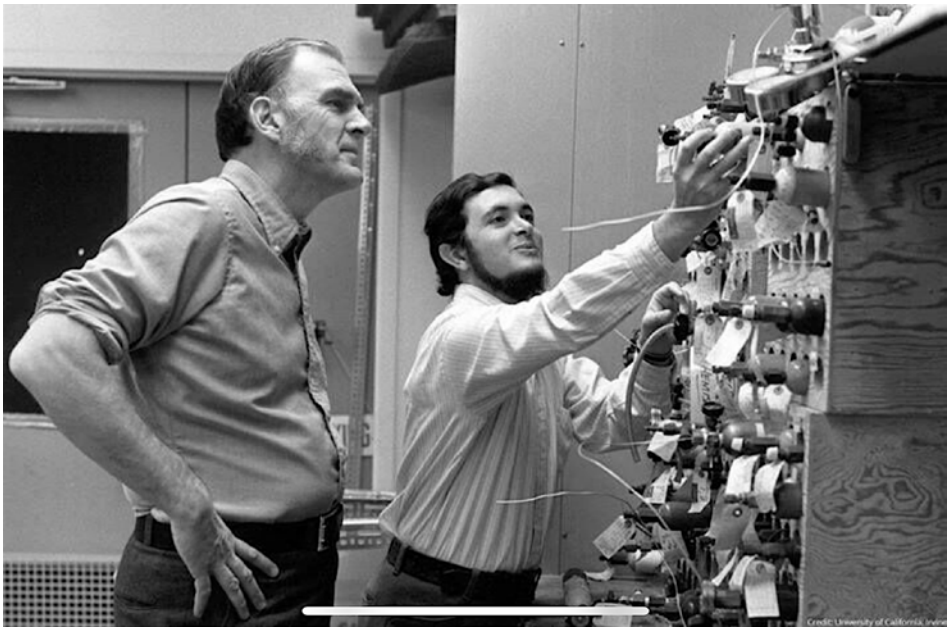


FIGURE 10.9: Sherry Rowland (left) and Mario Molina (right) in their laboratory at the University of California, Irvine. DR.

Northern Hemisphere in 1890 and again in 1929 by Carl Størmer (1874-1957) and were given the German name *Perlmutterwolken*. These clouds occur only episodically in the boreal regions, which are generally warmer than the southern polar regions, where these clouds are observed every year below 26 km altitude. This is precisely the altitude under which ozone is almost completely destroyed in September and October. Solomon hypothesized that the chlorine, which is mainly in the form of inert reservoirs (HCl and $ClONO_2$), is activated by reactions taking place on the surface of ice particles in the clouds. In the austral spring, when the atmosphere is illuminated by solar radiation, chlorine is present mainly in the form of the ClO radical that rapidly destroys significant amounts of ozone inside the polar vortex. The mathematical model developed by Rolando Garcia at the National Center for Atmospheric Research in Boulder, Colorado, and used by Solomon, showed that if the chlorine activation reactions on the ice particles do occur, stratospheric ozone should disappear within a few weeks below 26 km above the Antarctic continent. It remained to be shown by observation that Solomon's hypothesis was correct.

With this goal in mind, the U.S. agencies NASA, NOAA, and the National Science Foundation (NSF) pooled substantial financial resources to rapidly organize measurement campaigns in the South Pole region. The first campaign took place in September 1986, just two years after the publication of Farman's article. The second, more ambitious campaign began in August 1987. This time, NASA used the ER-2, a former spy plane converted into a research aircraft, to measure ClO and ozone concentrations at an altitude of 20 km. The plane flew in the lower stratosphere between the Puntas Arenas air base in Chile and a geographic point



FIGURE 10.10: Two pioneers in the discovery of the ozone hole: Susan Solomon (left) and Joseph Farman (right). © DR.

over Antarctica. The measurements left no doubt: as soon as it entered the polar vortex, the instruments on board measured a sudden and significant increase in ClO concentration and, at the same time, a significant deficit in ozone content. In other words, as Susan Solomon suggested in 1986, chlorine is indeed activated over Antarctica during the austral spring and is responsible for the phenomenal ozone depletion in this part of the world in September and October. Since the 1980s, chlorine, mainly of industrial origin, has been responsible for the formation of a hole in the ozone layer over the Antarctic continent. In 1987, Louisa and Mario Molina discovered the catalytic cycle of ozone destruction by chlorine in the polar regions. It should be noted that the polar regions of the Northern Hemisphere have been relatively unaffected by significant ozone depletion because the temperature of the stratospheric air masses in these regions is too high for

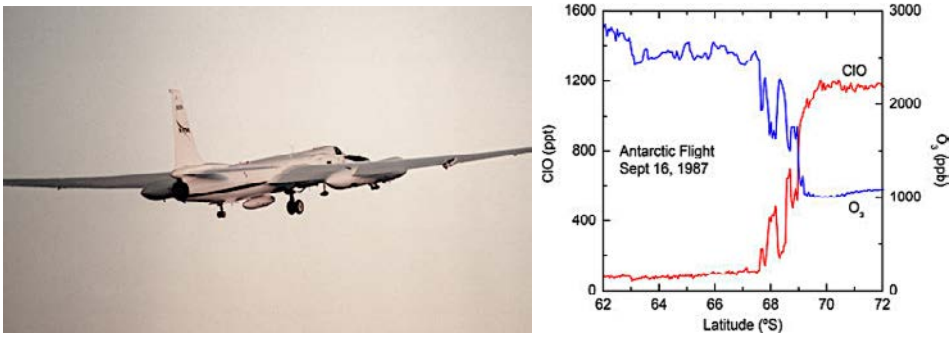


FIGURE 10.11: Left: NASA's ER-2 aircraft. Source: NASA Dryden Flight Research Center photo collection. At right: Ozone and ClO concentrations measured as a function of latitude at 20 km altitude on September 16, 1967. The aircraft enters the polar vortex (ozone hole region) at 69 degrees latitude. As the aircraft crosses this meteorological boundary, the instruments record a significant change in ClO and ozone concentrations. Source: Anderson, J.G., Brune W.H., and Proffitt M.H., *J. Geophys. Res.*, 94, 11465-11479, 1989.

clouds to form for a sufficiently long period of time. However, on rare occasions when the temperature inside the polar vortex is exceptionally low, anomalies in the ozone layer have been observed.

On September 16, 1987, under the auspices of the World Meteorological Organization and the United Nations Environment Programme, a protocol to protect the ozone layer was signed in Montreal by 46 nations and subsequently ratified by all UN member states and the European Union. In the years that followed, several more binding amendments to the Montreal Protocol were adopted, resulting in a global ban on the production of the main ozone-depleting substances. This was a real success for the scientific community, Sherry Rowland told a White House meeting on climate change in 1997:

> "Is it enough for a scientist simply to publish an article? Isn't the responsibility of scientists, if you believe that you have found something that can affect the environment, isn't it your responsibility to do something about it, enough so that action actually takes place? ... If not us, who? If not now, when?"

Despite this political success, and because CFCs will remain in the atmosphere for several decades, the ozone hole is not expected to disappear until about 2060.

Nuclear Winter

In the early 1980s, at the height of the Cold War between the United States and the Soviet Union, Paul Crutzen watched a huge forest fire burn in the foothills of the Rocky Mountains near Boulder, Colorado, where he lived. An idea occurred to him: if a global nuclear conflict were to occur, such fires would have to appear in many parts of the planet. The Earth would soon be surrounded by a huge layer of smoke. The effects of such a conflict on the atmosphere would be devastating, not only for the country being attacked but for the aggressor country as well. To investigate this question, Crutzen and his colleague John Birks, a professor at the University of Colorado, decided to study the effects of a hypothetical nuclear war on the Earth's environment, particularly on the ozone layer. This study, published in 1982 in the Swedish journal *Ambio*[336] (see Box 10.1) under the title "Twilight at Noon," indicated that the large amounts of smoke produced by the fires that would be generated during a nuclear confrontation could significantly disrupt the exchange of radiative energy in the atmosphere, prompting several researchers to study the consequences of nuclear explosions on the climate. In the United States, Richard Turco, Owen B. Toon, Thomas P. Ackerman, James B. Pollack, and Carl E. Sagan (1934-1996) showed in a 1983 article published in *Science*[337] that the smoke from burning cities and forests would block incoming sunlight from entering the atmosphere, significantly reducing Earth's surface temperatures and disrupting ecosystems and

[336] Crutzen, P.J., Birks, J.W., *Ambio, 11*, 114-125, 1982.

[337] Turco, R.P., Toon, O.B., Ackerman, T.P., Pollack, J.B., Sagan, C., Nuclear winter: Global consequences of multiple nuclear explosions. *Science, 222*, 1283-1292, 1983.

agricultural productivity. According to the mathematical models used at the time, this would plunge the Earth into a state of devastation with catastrophic consequences for human and natural systems. The article concludes:

> "Significant hemispherical attenuation of the solar radiation flux and subfreezing land temperatures may be caused by fine dust raised in high-yield nuclear surface bursts and by smoke from city and forest fires ignited by airbursts of all yields. For many simulated exchanges of several thousand megatons, in which dust and smoke are generated and encircle the earth within 1 to 2 weeks, average light levels can be reduced to a few percent of ambient and land temperatures can reach -15° to -25 °C. [...]
>
> When combined with the prompt destruction from nuclear blast, fires, and fallout and the later enhancement of solar ultraviolet radiation due to ozone depletion, long-term exposure to cold, dark, and radioactivity could pose a serious threat to human survivors and to other species."

In the same year, in Moscow, two researchers from the Computing Center of the Soviet Academy of Sciences, the Russian mathematicians Vladimir V. Aleksandrov and Georgiy L. Stenchikov published a remarkable article on the same topic[338]. Other notable scientists involved in the scientific debate included Steve Schneider, Starley Thompson of the National Center for Atmospheric Research, and Alan Robock of the University of Maryland. The theoretical foundations that led to the concept of nuclear winter were discussed, criticized, and refined, leading to a consensus on the plausibility of widespread cooling of the Earth's surface following a severe nuclear conflict.



FIGURE 10.12: Several of the key players in the early scientific studies of nuclear winter.

[338] Aleksandrov, V.V., Stenchikov, G.L., On the modeling of climatic consequences of the nuclear war. *Proceedings in Applied Mathematics*, Computing Centre, USSR Academy of Sciences, Moscow, 21 pp., 1983.

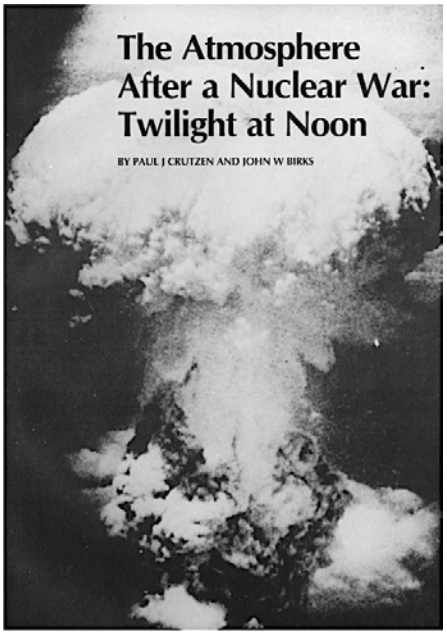


FIGURE 10.13: The first page of the article by Crutzen and Birks published in the Swedish magazine *Ambio* in 1982.

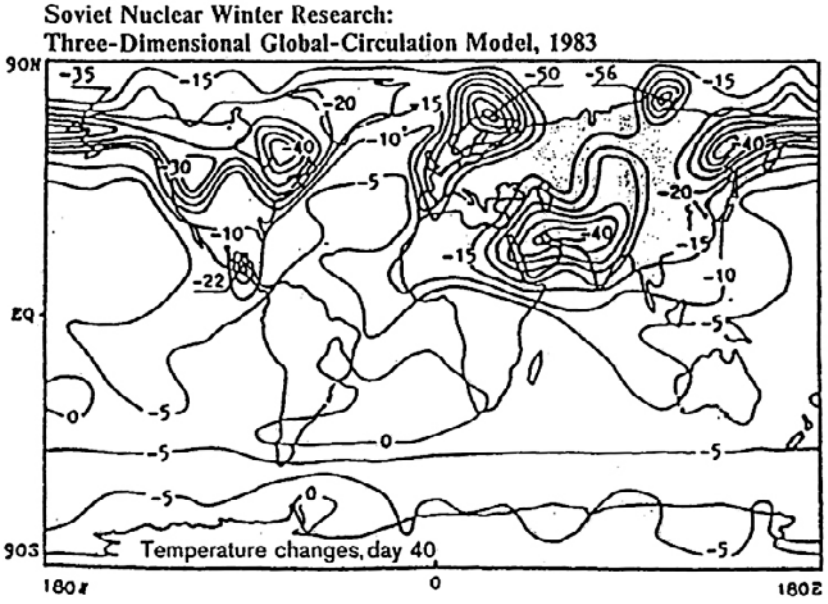


FIGURE 10.14: Global distribution of cooling (degrees Celsius) that would occur 40 days after the outbreak of a global nuclear war. Diagram presented at the International Seminar on Nuclear War in Erice, Sicily, Italy in 1984, based on the results of the mathematical model developed in the Soviet Union under the direction of Vladimir Alexandrov. Source: CIA.

Box 10.1. How the Concept of Nuclear Winter was Developed: the Viewpoint of John Birks, University of Colorado

It all began in 1981 with Jeannie Peterson, then editor of Ambio. Because of the arms race between the U.S. and the Soviet Union and the ongoing deployment of nuclear missiles in Eastern and Western Europe, Jeannie decided to edit a special issue of Ambio on the environmental effects of a nuclear war, and she recruited experts in various fields to contribute articles on different aspects, such as direct effects, effects on the land, on the oceans, on the atmosphere, on agriculture, and so on. Paul Crutzen was by then a very well-known atmospheric scientist, especially in Sweden, where he had worked, and he had published in Ambio before, so she invited him to write the article on the effects of nuclear war on the atmosphere.

The invitation came about the same time I arrived with my family to spend a sabbatical year working with Paul. Paul knew that, as a graduate student, I had published a paper with Hal Johnston and his postdoc Gary Whitten on the effects of past nuclear weapons testing on the ozone layer. This paper, and the one before it by Henry M. Foley and Malvin A. Ruderman, had led to the concern that a nuclear war would destroy the ozone layer by deposition of the NO produced in the nuclear fireballs in the stratosphere. (The purpose of the Foley and Ruderman paper was to show that past nuclear weapons testing hadn't affected the ozone layer, so SST shouldn't either destroy ozone).

These and subsequent papers, including one by Turco *et al*, led to a 1975 NAS study on the effects of nuclear war on the ozone layer, which was summarized in Jonathan Schell's 1982 book, *The Fate of the Earth*, around the same time as Crutzen-Birks paper. Although that book was a bestseller, it was out of date by the time it was published. Paul and I discovered what became known as the "nuclear winter" effect (named by Richard Turco, I believe), because our model calculations showed no significant ozone depletion. In fact, the model runs showed some ozone production in the lower stratosphere. This was because the baseline nuclear war scenario we were given to evaluate included only modern warheads resulting in smaller nuclear detonations, all with yields less than 1 Mt. As a result, very little NOx rose into the stratosphere, and the ozone depletion that occurred was more than offset by ozone production in the lower stratosphere.

The lack of ozone depletion for the baseline scenario (we also evaluated scenarios with the addition of multi-megaton weapons, which caused up to 50% ozone depletion) led us to focus on photochemical smog production in the troposphere. To do this, we needed to include organic emissions from the fires, so we searched the fire literature to estimate emissions from burning materials. Since most of the literature was based on observations of forest fires, we did our initial calculations based on burning forests. We decided to do some runs for emissions from burning 1 million square kilometers of forest – not that we thought that much forest would burn (although it could), but we wanted to account for other emissions from burning cities, oil storage, etc. It was an example calculation.

We did the model runs and got high tropospheric ozone, PAN, etc. throughout the northern hemisphere, as expected. Then it occurred to us that the smoke from the fires (the fire literature was full of smoke emission factors) might be blocking some of the sunlight and reducing the amount of photochemistry that was taking place. I remember doing this calculation in Paul's office on our handheld calculators, and that's when we discovered that for our 1000 km x 1000 km example calculation, anywhere from 50% to 99% of the sunlight would be blocked from reaching the Earth's surface.

At that point, we knew that the most important effect of nuclear war would be the loss of sunlight for crops and natural ecosystems, and the climate effects of most of the solar energy being absorbed in the atmosphere rather than at the ground. At that point, we flew to Stockholm to talk to Jeannie about the paper and let her know how consequential it would be if we were right. We wanted to make sure she was comfortable with it. We sent the paper out to about 25 scientists for our review and incorporated their comments in the final revision.

In the years that followed, questions about nuclear winter took on a political connotation in the context of arms control, an issue then at the center of negotiations among nuclear-armed countries. On February 12, 1985, the President of the United States, Ronald Reagan, spoke of a nuclear conflict in an interview with the *New York Times*:

> "A great many reputable scientists are telling us that such a war could just end up in no victory for anyone because we would wipe out the earth as we know it."

However, against the backdrop of the international tensions of the time, a dramatic event occurred that has not been resolved to this day. In March 1985, Vladimir Aleksandrov went to Cordoba, Spain, to participate in the Second International Conference on Nuclear Free Zones, where he was invited to present his work by the Communist mayor of the city. It is believed that he left for Madrid after the meeting. He has not been seen since. His personal belongings disappeared from his hotel room, and his passport was found in a city trash can. We don't know what happened to him, but several hypotheses have been advanced. Was he kidnapped by the KGB and returned to his country? Or, as the

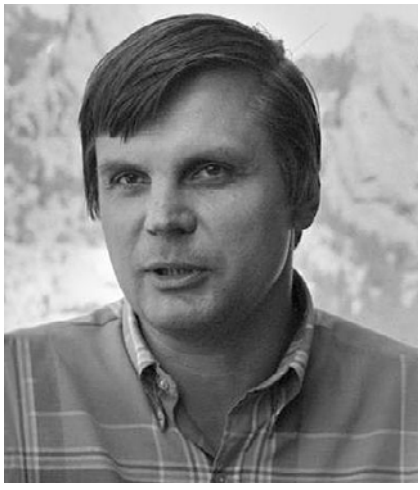


FIGURE 10.15: Vladimir V. Aleksandrov photographed in Boulder, Colorado, in front of the Rocky Mountains.

Italian historian Guila Rispoli[339] suggests, was he the victim of an operation by the CIA, which was far more concerned about Aleksandrov's activities than the USSR? Aleksandrov had the support of the USSR government, traveled freely in the U.S., and even had access to NCAR's supercomputers in Boulder. In any case, the mystery remains.

In the year 2000, Mikhail Gorbachev (1931-2022), who was president of the Soviet Union from 1985 to 1991, referred to the issue of nuclear winter[340]:

> "Models made by Russian and American scientists showed that a nuclear war would result in a nuclear winter that would be extremely destructive to all life on Earth; the knowledge of this was a great stimulus for us, people of honor and morality, to act in this situation."

The scientific work continued in the following years. As climate models became more sophisticated and the atmospheric processes involved were better understood, the initially very alarmist climate projections were revised to show that the cooling was likely to be less than originally thought; talk turned to nuclear autumn. In any case, even if the initial scenarios had to be tempered, the impact of the research on understanding climate dynamics and the influence of these studies on international nuclear policy were significant.

Microplastics

The history of plastics began in New York City. It was in this city, the cradle of economic development at the time, that Michael Phelan (1819-1871), an Irish-born billiard player who became a true champion of the sport, settled. Phelan himself manufactured and sold billiard equipment, but he soon faced the question of whether the expensive elephant ivory balls used in the sport would be available in the future. In response to a competition Phelan launched to find an innovative alternative, a young American engineer, John Wesley Hyatt (1837-1920), proposed the use of Parkesin, a mixture of nitrocellulose and camphor developed in 1802 by Alex Parkes (1813-1890), a metallurgist from Birmingham, England. Today, this material is the first plastic ever produced. But it was in Belgium that a Ghent chemist named Leo Hendrik Baekeland (1863-1944) discovered another material that was used in a wide range of industrial and domestic applications, replacing more traditional materials such as metals. Baekeland emigrated to the United States in 1889 after receiving his doctorate in his native Ghent, Belgium. In 1909, he developed "Bakelite", a moldable material based on a resin of phenol and formaldehyde. It solidified when it cools after having been heated. In the years that followed, industry developed very attractive analogues, particularly in the form of polyethylene and polystyrene. This has been a great industrial success (today, almost 450 million tons of plastic are produced worldwide every year), but with disastrous consequences for the environment:

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339 *From the Cold War to Global Warming.*

340 Hertsgaard, M., Mikhail Gorbachev explains What's rotten in Russia, *Salon.com.* 2023. https://www.salon.com/2000/09/07/gorbachev/.

less than 10% of the plastic used is recycled. Once in nature, plastic degrades through photodegradation and thermo-oxidation under the influence of ultraviolet light and heat from the sun. The action of water on the polymer molecules causes the plastic to break down into smaller and smaller particles, some of which are released into the atmosphere. The result is an increasing number of microparticles (smaller than 5 millimeters) and even nanoparticles (smaller than 1 micrometer) in the air.

Microplastic particles also result from the wear and tear of materials, particularly synthetic textiles, car tires, certain paints, and plastic packaging. They are either released directly into the atmosphere or carried by wastewater into rivers and oceans. Once in the air, they disperse before settling on continental and oceanic surfaces. Today, an estimated 10 million tons of microplastics are dumped into the ocean each year. Finer particles disperse far from where they are dumped into the atmosphere. Some fall to the surface of polar regions and become trapped in ice. Little is known about the effects of microplastics on human health. However, we do know that these particles are ingested by marine mammals, fish, and birds. This is how they enter the food chain and are consumed by humans. Microplastics are also found in tap water, bottled water, and other beverages.

According to the World Health Organization (WHO), there is currently little evidence that microplastics cause significant adverse health effects. However, it has been suggested that these particles, once inhaled or ingested by humans, may stimulate the release of endocrine disruptors. They could also cause oxidative stress, DNA damage, organ dysfunction, metabolic disorders, and disrupt the immune response. They could also affect reproduction and development. Epidemiological data also suggest that certain chronic diseases are associated with exposure to microplastics. Finally, microplastics can carry other chemicals, particularly heavy metals and organic pollutants, posing a further threat to human health.

11
Climate Change

Climate change has always fascinated people in all parts of the world, although the concept of climate has evolved over time. The origin of the word "climate" can be traced back to ancient Greece, where the term "κλιμα" (*climate*) means inclination, slope, and refers to the inclination of the Earth's axis of rotation. The value of this parameter was determined as early as the third century BCE by the geographer Eratosthenes (~276-~195/194 BCE). The mathematician Ptolemy (~100-~170 CE), inspired by the ideas of Eratosthenes, defined "κλιματα" as a succession of zones surrounding the Earth between the equator and the poles, determined by the obliquity of the sun's rays. The "κλιμα" of the ancient Greeks referred to different geographical regions of the world characterized by very different natural environments. The term was adopted by the Latin language as *clima,* then by medieval French and English as *climat* and *climate*, respectively. The French *Littré* dictionary defines climate as "the space between two circles parallel to the Earth's equator on maps and charts". And the dictionary adds that, more broadly, a climate is "a stretch of land in which the temperature and other atmospheric conditions are almost identical everywhere". This second definition, which includes meteorological characteristics, thus represents an evolution of the original concept that emerged as the first explorers traveled the world and encountered widely varying atmospheric conditions, even at similar latitudes.

In the nineteenth century, environmentalist Alexander von Humboldt (1769-1859) defined climate as "the combination of caloric, aqueous, luminous, aerial and electric phenomena that give this land its meteorological character, different from that of another country situated at the same latitude and under the same geological conditions". During this century, geologists collected a series of "witnesses" that suggested the existence of slow, natural variations in climate, with cold periods following warmer ones. This concept, promoted by the Swiss naturalist Louis Agassiz (1807-1873), was not universally accepted at first. It wasn't until more physical evidence and geological samples were examined that the ice age theory was finally accepted. New research then focused on the Quaternary period, the 2.58-million-year sequence of glacial and interglacial periods. At the end of the nineteenth century, scientists feared the arrival of a new "planetary winter" that would profoundly affect the planet and especially the populations of northern Europe and the Americas for thousands of years. Some scientists

were even thinking of intervening to counteract this threat. The idea would be to burn all the coal in the mines, thereby increasing the greenhouse effect.

In the twentieth century, research evolved again, with the analysis of geological and glaciological data highlighting the global nature of the climate system. Variations in the planet's average temperature thus served as an indicator of climate change. Moreover, when one talks about the impact of human activities, one often refers to "global warming," when one should be considering many other effects. Today, the World Meteorological Organization (WMO) defines climate as the measurement of the mean and variability of quantities such as temperature, precipitation, or wind over periods ranging from a few months to thousands or even millions of years. The regional and even local nature of climatic variations is considered to better describe the impact of global changes on society. Research focuses on the response of planetary components to natural and anthropogenic climate forcings, with a special interest in the nonlinear behavior of the terrestrial system. Attention is given to the identification of tipping points that could lead to large-scale effects, probably catastrophic for our societies.

From Antiquity to the Industrial Revolution

As early as the fourth century BCE, Greek philosophers were interested in climate disruption. In his *Meteorologica*, Aristotle pointed out that places that once enjoyed a good climate were becoming less pleasant:

> "This is what happened in Greece to the land of Argos and Mycenae. At the time of the Trojan War, Argos was swampy and could support few inhabitants, while Mycenae was good land and therefore the most famous region. Now it's the opposite [...] for Mycenae has become unproductive and completely dried out, while the Argian land that was once swampy and unproductive is now agricultural land. What happened in this small district can therefore be assumed to happen to large districts and whole countries."

Theophrastus was interested in the effects of human activity on climate. This student of Aristotle and his successor in the Peripatetic School[341], who is sometimes considered the father of ecology and author of *De causis plantarum* (On the Etiology of Plants), noted that in Larissa, in the region of Thessaly, Greece,

> "The waters were abundant and the whole region resembled a swamp. However, after the waters were drained and measures taken to prevent a renewal of their stagnation, the region became colder and frosts occur more frequently [...]. The olive trees, which were once large and beautiful around the town, no longer exist, and the wine, which was never affected by the cold before, is now frequently damaged."

[341] *The Peripatetic school was* an informal philosophical school founded by Aristotle in 335 AED at the Lyceum of Athens.

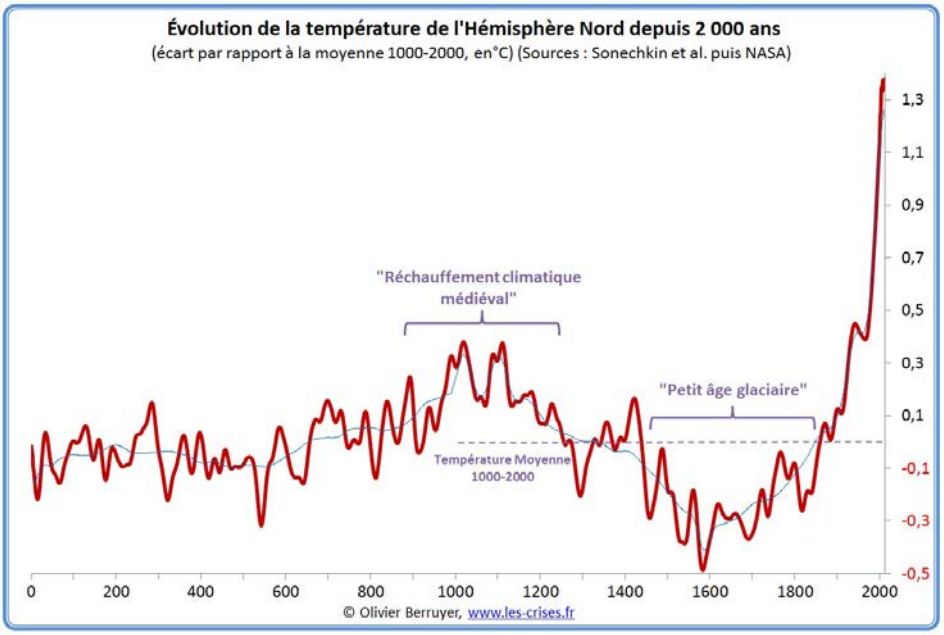


FIGURE 11.1: Evolution of mean temperature anomalies in the Northern Hemisphere reconstructed over the last 2000 years. Note the medieval climate optimum around 1000 and the Little Ice Age between 1400 and 1800. Finally, there is a significant increase in temperature from 1850 onwards. © Olivier Berruyer.

During the Roman period, the climatic upheavals were associated with intense deforestation, which, in addition to the collection of firewood, made possible the development of agriculture, the construction of temples and palaces, and the use of military equipment. Between 250 and 400 CE, an unusually hot period occurred in the Mediterranean region, but this warming, perhaps partly of human origin, was mitigated by the presence in the atmosphere of large quantities of fine particles produced by the gigantic fires that accompanied the destruction of the forest. This Roman climatic optimum was followed between 536 and 660 CE by a colder period caused by several large volcanic eruptions (536, 541, and 547), which have probably contributed to the fall of the Roman Empire.

Between the tenth and fourteenth centuries, temperatures were relatively mild (Medieval Climatic Optimum), but from the fourteenth to nineteenth centuries, they were significantly lower (Little Ice Age). During this period, winters were cold and long, as evidenced by the paintings of several medieval artists, notably Pieter Breughel the Elder (1525/1530-1569).

In the Middle Ages and even during the Renaissance, concerns about climatic variations were initially regional or local in nature. This changed in the 18th century, when several scholars began to view climate as a phenomenon affecting the entire planet. In his *Theory of the Earth*, published in 1749, Georges Louis Leclerc, comte de Buffon (1707-1788), director of the Jardin du Roi in France (now the Jardin des Plantes in Paris), invoked the formation of

planets to explain the evolution of global climate. For him, planets were pieces of the sun torn from the central star by collisions with comets. And in 1778, in his *Epochs of Nature,* he added that the Earth, initially molten, has cooled progressively and eventually reached a state of glaciation incapable of any biological production. Finally, based on measurements of the cooling rate of iron, he estimated the age of the Earth to be about 75,000 years.

This theory of gradual global cooling was condemned by the Sorbonne. It was also condemned by the English naturalist and historian Theodore Augustine Mann (1735-1809), a Carthusian priest[342] who believed, on the contrary, that the earth was gradually warming and that this warming was global and irreversible. Abbé Mann, who became the Perpetual Secretary of the *Académie Impériale et Royale des Sciences et Belles-Lettres* in Brussels in 1787, was interested in meteorological phenomena and made numerous observations of atmospheric conditions under the auspices of the Académie. To understand how the climate had evolved in the past, he studied ancient literature, particularly the works of Greek and Roman authors. These writers emphasized the extreme severity of winters in Europe, with rivers and lakes freezing over for long periods. In his *Mémoires sur les grandes gelées* of 1792, he wrote

> "It therefore seems incontestable that the soil and temperature of all countries, from Spain to the Indies, and from Mount Atlas to Lapland and the far north, have changed entirely over the centuries, from the first historical monuments we have of them, to the present day, gradually moving from extreme humidity and cold, to great dryness and heat, that is, from one to the other."

Was Abbé Mann a forerunner of the global warming theory, as Muriel Collard[343] claims? Yes, to a certain extent, since the priest was perhaps the first to recognize the global nature of climate change. But unlike contemporary climatologists, he attributed the origin of climate change primarily to natural phenomena rather than to human activity, even though the latter may have accelerated the warming process.

A Climate Change Survey in France

Human activity, particularly deforestation, was increasingly cited in the early nineteenth century to explain what was perceived in Europe as a cooling rather than a warming trend. An interesting initiative was taken by the French

[342] Mann left England in 1756 at the outbreak of the Seven Years' War with France, taking refuge first in Spain. In 1758, he joined the *Sheen Anglorum* convent in Nieuport, Belgium, a religious community of exiled English Carthusian monks. A year later, he was ordained a priest and stayed at the monastery for nineteen years. Between 1787 and 1794, he held the post of Secrétaire Perpétuel at the *Académie de Bruxelles* and made numerous meteorological observations under its auspices. The French invasion of Belgium in 1794 forced Mann to leave the country and, after traveling in Germany and England, he finally settled in Prague, where he continued his literary work until his death in 1809.
[343] Muriel, C., Mann, T., *Savoir et pouvoir. Un théoricien du climat à l'académie de Bruxelles au XVIIIe siècle*, Regards, Académie Royale de Belgique, Vol. 6, 222 pp., 2022.

government at the time of the monarchical Restoration. On April 25, 1821, Louis XVIII's Minister of the Interior, Count Joseph-Jérôme Siméon (1749-1842), asked the departments to investigate the possible causes of the climatic disturbances that had apparently been occurring for several years. In a memorandum sent to all departmental prefects, the minister wrote

> "Gentlemen, for some years now, we have been witnessing noticeable cooling in the atmosphere, sudden variations in the seasons, and extraordinary hurricanes or floods to which France seems to be becoming increasingly prone. This is partly attributed to the deforestation of mountains and forests, the lack of shelter in the countryside, and the absence of natural obstacles to the north and west winds and clouds. The same causes would produce the same effects throughout Europe, and these phenomena would be worthy of attention everywhere. These evils would not be without remedy, and it would be important that, particularly in France, measures be taken to avert the inconveniences and misfortunes whose principle would have been recognized."

Indeed, the cooling observed in France at the beginning of the nineteenth century coincided with significant deforestation in the country. France's forests were heavily exploited to build warships and, during the Restoration, to pay off the national debt through timber sales. But did this intense deforestation explain the unusually low temperatures observed in the few years after Napoleon's fall?

The results of the survey were inconclusive. Only 42 departments responded, many of them complaining that they had to answer yet another question they considered unimportant. Fourteen departments, however, thought that deforestation was indeed causing the air and soil to cool, but thirty-nine disagreed. Thirty-two departments note that winters have become colder and longer, but twenty-one disagree. Finally, twenty-seven departments stated that the winds had become more violent, while twenty-six others thought this was not the case. A committee of the Royal Academy of Sciences in Paris, charged with examining the results of the survey, concluded in February 1824 that it had "found neither sufficiently positive nor sufficiently complete evidence of the disputed facts to enable it to form an opinion".

We now know that the relatively cold period that occurred during this time, and particularly the crop failures of 1816-1817, were probably less related to deforestation than to the eruption of the Tambora volcano on the island of Sumbawa (Indonesia) in 1815. During this extremely violent episode, volcanic particles injected into the atmosphere up to an altitude of 45 km were responsible for the global cooling of the planet.

Svante Arrhenius and Guy Callendar

At the end of the nineteenth century, an important event took place in Sweden. In Stockholm, the Swedish physicist and chemist Svante August Arrhenius (1859-1927) became interested in the influence of atmospheric carbon dioxide on the Earth's surface temperature. Arrhenius was highly respected by his peers.

He was considered to be one of the fathers of physical chemistry, and his doctoral thesis, for which he received a very average grade from his professors at Uppsala University, showed that crystalline salts, when dissolved in water, split into pairs of positive and negative charges; these ions generate an electric current that accompanies the electrolysis of water. Arrhenius also showed that reactions in the aqueous phase involve these ions. Despite the reluctance of his professors at Uppsala, he received support from foreign colleagues who noticed the originality of his work and invited him to visit their laboratories. In 1895, he was appointed professor at the Stockholm Högskola, where he became rector in 1897. He was elected to the Royal Swedish Academy of Sciences in 1901, despite fierce opposition from some of its members, and was awarded the Nobel Prize in Chemistry in 1903 for his work on ion theory.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

APRIL 1896.

XXXI. *On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground.* By Prof. SVANTE ARRHENIUS *.

I. *Introduction: Observations of* Langley *on Atmospherical Absorption.*

A GREAT deal has been written on the influence of the absorption of the atmosphere upon the climate. Tyndall † in particular has pointed out the enormous importance of this question. To him it was chiefly the diurnal and annual variations of the temperature that were lessened by this circumstance. Another side of the question, that has long attracted the attention of physicists, is this: Is the mean temperature of the ground in any way influenced by the presence of heat-absorbing gases in the atmosphere? Fourier‡ maintained that the atmosphere acts like the glass of a hot-house, because it lets through the light rays of the sun but retains the dark rays from the ground. This idea was elaborated by Pouillet §; and Langley was by some of his researches led to the view, that "the temperature of the earth under direct sunshine, even though our atmosphere were present as now, would probably fall to −200° C., if that atmosphere did not possess the quality of selective

* Extract from a paper presented to the Royal Swedish Academy of Sciences, 11th December, 1895. Communicated by the Author.
† 'Heat a Mode of Motion,' 2nd ed. p. 406 (Lond., 1865).
‡ *Mém. de l'Ac. R. d. Sci. de l'Inst. de France*, t. vii. 1827.
§ *Comptes rendus*, t. vii. p. 41 (1838).

FIGURE 11.2: Svante Arrhenius (left) and the first page of the article on the effect of CO_2 on surface temperature (right).

Around 1895, Arrhenius began to study the cycles that determine ice ages. At that time, the reasons for the appearance of these periods were a mystery that geophysicists were unable to solve. The explanation undoubtedly lay in the theory of climatic variability developed by the Scottish scientist James Croll (1821-1890), which was based on variations in the Earth's orbit. Inspired by these studies, Arrhenius believed that the atmosphere played an important role in determining long-term variations in climate. This led him to investigate the role of carbon dioxide. Building on earlier work by Fourier, Tyndall, Pouillet,

Langley, and Ångstrøm, he determined the amount of heat trapped by CO_2 and water vapor in the atmosphere. In his resounding 1896 paper[344] he wrote

> "The air retains heat (light or dark) in two different ways. On the one hand, the heat suffers a selective diffusion on its passage through the air; on the other hand, some of the atmospheric gases absorb considerable quantities of heat. These two actions are very different. [...] The selective absorption of the atmosphere [...] is not exerted by the chief mass of the air, but in a high degree by aqueous vapor and carbonic acid, which are present in the air in small quantities.[...] The influence of this absorption is comparatively small on the heat from the sun, but must be of great importance in the transmission of rays from the earth. Tyndall held the opinion that the water-vapor has the greatest influence whilst other authors [...] are inclined to think that the carbonic acid plays the more important part. The researches of Paschen[345] show that these gases are both very effective, so that probably sometimes the one, sometimes the other, may have the greater effect according to the circumstances."

Arrhenius concluded that "if the amount of carbon dioxide increases geometrically, the temperature must increase almost linearly". He then calculated the warming that would result from an increase or decrease in atmospheric CO_2. His calculation took into account the influence of water vapor: the warming caused by an increase in CO_2 leads to increased evaporation of water from the surface of the oceans and thus to an increase in humidity. The result is an increase in the greenhouse effect. However, Arrhenius ignored other effects, such as the adjustment of cloud cover, changes in heat exchange through atmospheric convection, changes in the biosphere, and so on. In his 1896 article, he concluded that a doubling of CO_2 would warm the planet by 5 to 6 °C, while a tripling would warm it by 7 to 9 °C. Reducing CO_2 by a third of its atmospheric concentration would result in a cooling of about 3 °C. In the following years, Arrhenius developed his calculations further and arrived at slightly different values: 4 °C for a doubling of CO_2 and 8 °C for an increase by a factor of 4. These results were not very different from those obtained today by complex mathematical climate models. What we call *climate sensitivity*, i.e., the average warming of the planet for a doubling of atmospheric CO_2, is now estimated to be between 2 and 6 °C, depending on the model, in good agreement with the 4 °C derived by Arrhenius.

It should be noted that Arrhenius, in his work of 1896, introduced the concept of sequestration by the ocean of a fraction of the CO_2 emitted into the atmosphere:

> "The ocean [...] plays an important role as a regulator of the quantity of carbonic acid in the air by means of the absorptive power of its water, which gives off carbonic acid as its temperature rises and absorbs it as it cools."

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[344] Arrhenius, S., On the influence of carbonic acid in the air upon the temperature of the ground. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 41*(251), 237-276, 1896, https://doi.org/10.1080/14786449608620846.

[345] Louis Carl Heinrich Friedrich Paschen (1865-1947), German physicist and President of the Physikalisch-Technische Reichanstalt in Berlin from 1924 to 1933. He was dismissed in 1933 as an opponent of the Nazi regime under the Law for Restoration of the Professional Civil Service.

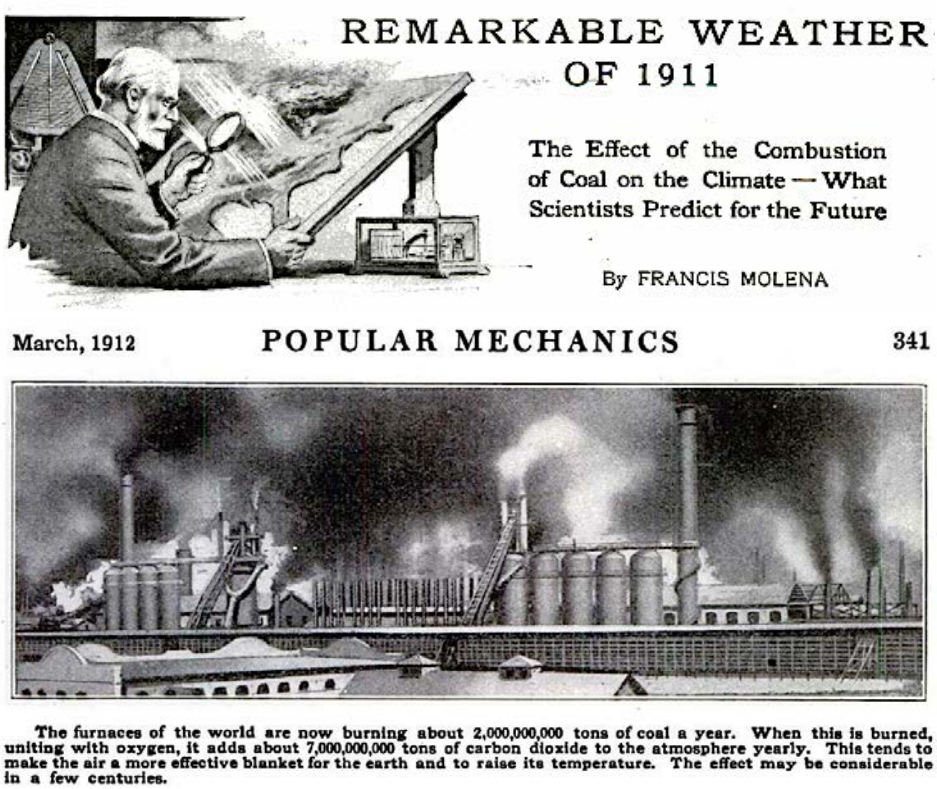
This view was confirmed in 1899 by the American geologist Cyrus F. Tolman (1873-1942), who established the relationship between carbon dioxide in the ocean and carbon dioxide in the atmosphere[346]. He concluded that the ocean contains eighteen times more CO_2 (in the form of carbonic acid) than the atmosphere. He noted, however, that the solubility of this gas varies with temperature and that global warming could alter the ocean's ability to absorb atmospheric CO_2.

By the beginning of the twentieth century, it had become clear that an increase in the amount of CO_2 in the atmosphere, coupled with the rapid development of industrial society, could lead to global warming. On March 12, 1912, the magazine *Popular Mechanics*, founded in New York in 1902, wrote[347]:

"The annual burning of two billion tons of coal worldwide results in an annual emission of 7 billion tons of CO_2."

The magazine added:

"This tends to make the air a more effective blanket for the Earth and raise its temperature. The effect may become considerable in a few centuries' time."



REMARKABLE WEATHER OF 1911

The Effect of the Combustion of Coal on the Climate — What Scientists Predict for the Future

By FRANCIS MOLENA

March, 1912 POPULAR MECHANICS 341

The furnaces of the world are now burning about 2,000,000,000 tons of coal a year. When this is burned, uniting with oxygen, it adds about 7,000,000,000 tons of carbon dioxide to the atmosphere yearly. This tends to make the air a more effective blanket for the earth and to raise its temperature. The effect may be considerable in a few centuries.

FIGURE 11.3: Press clippings showing the effects of industrialization on the atmosphere in the early twentieth century.

[346] Tolman, C.F., The carbon dioxide of the ocean and its relations to the carbon dioxide of the atmosphere. The *Journal of Geology,* 7 (6), 585-618, 1899.

[347] The article was reprinted in the August 14, 1912 edition of the New Zealand newspaper *Waitemata and Kaipara.*

The argument was taken up in scientific circles and, in 1914, the geophysicist Alphonse Berget (1860-1933), professor at the Oceanographic Institute (founded by Prince Albert I of Monaco), wrote in his book under the title "*Les problèmes de l'Atmosphère*" (The problems of the atmosphere):

> "The carbonic acid content of the atmosphere, after having decreased, seems to be increasing. This is understandable, for on the one hand, volcanic activity seems to be on the rise again, and in the present era is reaching a veritable paroxysm; on the other, industry is expanding at a prodigious rate. Until mankind has harnessed all natural forces - winds, waterfalls, ocean waves and tides - to serve his needs, his source of energy is the combustion of coal and oil, which he extracts from the earth's crust until the deposits are exhausted. But this combustion, with its ever-multiplying hearths, discharges considerable quantities of carbonic acid into the air, thus considerably increasing the dose of this gas.
>
> We can therefore assume that, for a few eons, even centuries, carbonic acid, more abundant in the atmosphere, will maintain a milder temperature, resulting in richer vegetation and more abundant harvests."

A few years later, in 1924, the American ecologist Alfred James Lotka (1880-1949), a specialist in population dynamics who moved from Austria-Hungary, warned of the CO_2 emissions associated with industrial development:

> "The great industrial era is founded upon, and the present day inexorably dependent upon, the exploitation of the fossil fuel accumulated in the past geological ages. Economically, we are living on our capital; biologically we are radically changing the complexion of our share in the carbon cycle by throwing into the atmosphere, from coal fires and metallurgic furnaces, ten times as much carbon dioxide as in the natural biological process of breathing. These human agencies alone double the amount of carbon dioxide in the entire atmosphere."

Because he was interested in glacial cycles, Arrhenius noted that CO_2 emissions resulting from human activity should be able to prevent mankind from entering a new Ice Age. In his book on the future of the world, published in 1906[348], he was optimistic and wrote:

> "We often hear lamentations that the coal stored up in the earth is wasted by the present generation without any thought of the future, and we are terrified by the awful destruction of life and property which has followed the volcanic eruptions of our days. We may find a kind of consolation in the consideration that here, as in every other case, there is good mixed with the evil. By the influence of the increasing percentage of carbonic acid in the atmosphere, we may hope to enjoy ages with more equable and better climates, especially as regards the colder regions of the earth, ages when the earth will bring forth much more abundant crops than at present, for the benefit of rapidly propagating mankind."

[348] *Väldarnas utveckling* translated into German (*Das Werden der Welten*, 1907) and English (*Worlds in the Making*, 1908)

Arrhenius' work is significant because the Swedish scientist was the first to quantify the relationship between increasing CO_2 emissions from the burning of fossil fuels and the climate. His calculation is truly the first climate model, and the results he produced still seem very realistic today.

In the United States, the geologist Thomas Chrowder Chamberlin (1843-1928), who was interested in the mechanisms responsible for global changes such as glaciations, turned his attention to the carbon cycle in the Earth system. Starting in 1896, this professor at the University of Chicago, head of the geology department, offered his students courses on *Methods of Work in Geology*. In his lectures, he discussed the climatic changes that had occurred throughout the history of the planet. Taking note of Arrhenius' recent work and considering that the CO_2 content of the atmosphere must have varied considerably over geological time, he presented some of the factors that determine the exchange of carbon between the atmosphere and the continental surface (volcanism, erosion, coal and limestone formation) and identified the various carbon reservoirs (atmosphere, ocean, biosphere, continents) in the terrestrial system. In a paper[349] published in 1897, he added that variations in the atmospheric concentration of CO_2, amplified by the effect of water vapor, should lead to climatic changes, and in particular to the advance or retreat of glaciers. For Chamberlin, the existence of glacial cycles was therefore directly linked to variations in the atmospheric concentration of CO_2.

Despite the interest and relevance of Arrhenius and Chamberlin's theories, dissenting voices were heard. Paleontologist Charles Schuchert (1858-1942), a professor at Yale University in Connecticut, claimed in 1919 that much of the CO_2 comes from volcanic eruptions[350]. And since volcanic activity will decrease in the future as part of planetary evolution, one should expect a gradual decrease in atmospheric CO_2 levels and thus the inevitable disappearance of life on Earth.

A few years after Arrhenius's resounding discovery, the idea that CO_2 influences climate was losing its appeal. Spectral measurements made in the laboratory by Anders Jonas Ångström[351] (1814-1874) in Sweden seemed to indicate that atmospheric attenuation of infrared radiation in the absorption bands of CO_2 is total. In other words, an increase in CO_2 should not lead to an increase in the amount of radiative energy trapped by the atmosphere. This saturation effect, therefore, called into question the role of carbon dioxide in global warming. The theory evoking the relationship between CO_2 and climate, therefore, fell into disuse for several decades.

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[349] Chamberlin T. C., A group of hypotheses bearing on climate changes. *The Journal of Geology, 5*(7), 1897.

[350] Schuchert, C. in Barell *et al.* (eds), *The Evolution of the Earth and its Inhabitants*, Yale U. Press, New Haven, CT.

[351] Son of Swedish spectroscopist Anders Jonas Ångström (1814-1874).

In a letter to Charles Schuchert[352], dated October 27, 1913, Chamberlin regretted his adherence to Arrhenius' theory[353]:

> "I have no doubt that you may be correct in thinking that the number who accept the CO_2 theory is less now than a few years ago. The original suggestion of Tyndall that a deficiency of CO_2 might be the cause of the glacial period received little attention and seems to have been so nearly forgotten that when Arrhenius made a similar claim it seemed to most scientists new and original and as it seemed to be founded on mathematical deductions from Langley's observations and to come with a high authority, it drew a large following. Unfortunately, however, Arrhenius' deductions from Langley's observations appear to have been unwarranted and when this was discovered a reaction was inevitable. [...] I greatly regret that I was among the early victims of Arrhenius' error."

In 1931, the American ionospheric geophysicist Edward Olson Hulburt (1890-1982), a former student of John Hopkins University who worked during 31 years at the US Research Naval Laboratory refuted Ångström's conclusions. When he took into account the amplifying effect of water vapor, he showed that doubling the amount of CO_2 in the atmosphere should result in a warming of 4 degrees Celsius.

The controversy attracted the attention of Guy Stewart Callendar (1898-1964), an English engineer specializing in steam turbine thermodynamics. Callendar, who was working with the support of the British Electrical and Allied Industries Research Association, became interested in the climate problem and worked on it during his spare time. In an article[354] published in 1938, this "amateur researcher" put the CO_2 atmospheric problem back on the agenda:

> "It is well known that the gas carbon dioxide has certain strong absorption bands in the infra-red region of the spectrum, and when this fact was discovered some 70 years ago it soon led to speculation on the effect which changes in the amount of the gas in the air could have on the temperature of the earth's surface. In view of the much larger quantities and absorbing power of atmospheric water vapor it was concluded that the effect of carbon dioxide was probably negligible, although certain experts, notably Svante Arrhenius and T. C. Chamberlin, dissented from this view."



FIGURE 11.4: Guy Callendar.

[352] Chamberlin to Schuchert, October 27, 1913, T.C. Chamberlin Papers, Department of Special Collections, Joseph Regenstein Library, Univ. of Chicago, addenda 3.5.

[353] See also Fleming, J.R., Chamberlin, T.C., Climate change, and cosmogony. *Studies in History and Philosophy of Modern Physics, 31*(3)3, 293-308, 2000.

[354] Callendar, G.S., The artificial production of carbon dioxide and its influence on temperature. *Quarterly Journal of the Royal Meteorological Society, 64* (275), 223-240, 1938.

Callendar was a modest and disinterested man who was much appreciated by his colleagues. He decided to systematically examine temperature measurements taken on the continent worldwide. He found that the Earth's average temperature had risen in tandem with the atmospheric concentration of carbon dioxide. From the observations available to him, he deduced that the sensitivity of the climate to a doubling of CO_2 was of the order of 2 °C, i.e. somewhat lower than the value calculated by Arrhenius on the basis of theoretical considerations.

Did Callendar's observational statistical relationship reflect a real physical relationship, or was it just a coincidence? In any case, the importance of CO_2 for climate was rediscovered in 1938 and, with Arrhenius' work forgotten, the term "*Callendar effect*" was coined to describe global warming due to the greenhouse effect of carbon dioxide.

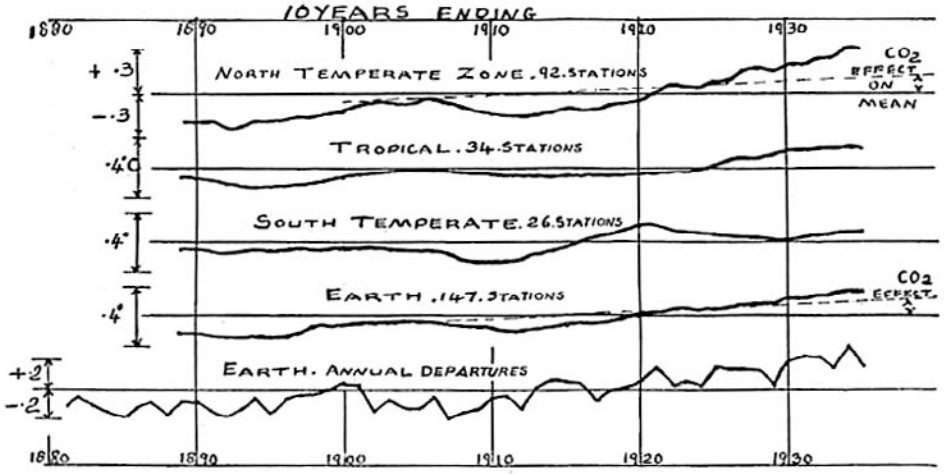


FIGURE 11.5: Temperature variations in different regions of the world and the deviation between 1880 and 1935 of the global mean temperature from its 1901-1930 average. Data established by Guy Callendar.

Callendar ended his 1938 article with the following sentences:

> "In conclusion it may be said that the combustion of fossil fuel, whether it be peat from the surface or oil from 10,000 feet below, is likely to prove beneficial to mankind in several ways, besides the provision of heat and power. For instance, the above-mentioned small increases of mean temperature would be important at the northern margin of cultivation, and the growth of favorably situated plants is directly proportional to the carbon dioxide pressure: In any case the return of the deadly glaciers should be delayed indefinitely. As regards the reserves of fuel, these would be sufficient to give at least ten times as much carbon dioxide as there is in the air at present."

Callendar saw the greenhouse effect as a beneficial phenomenon for humanity. Other scientists, however, feared that emissions from booming industry would lead to undesired global warming. This was the case with several nuclear physicists

who, after working on the Manhattan Project to develop the atomic bomb, were now advocating the development of uranium-fired power plants that would produce electrical energy without releasing CO_2 in the atmosphere (Box 11.1).

In 1953, Canadian physicist Gilbert Norman Plass (1920-2004), a graduate of Harvard and Princeton universities who had worked successively at the metallurgy department of the University of Chicago, at John Hopkins University in Baltimore, and at the Ford Motor Company, where he headed the theoretical physics department, said in an interview with *Time* magazine (May 25, 1953):

> "At its present rate of increase, CO_2 in the atmosphere will raise the Earth's average temperature by 1.5 °Fahrenheit every 100 years [...] For centuries to come; if man's industrial growth continues, the Earth's climate will continue to grow warmer."

Based on calculations he made on a rudimentary computer of the time, Plass predicted that a doubling of atmospheric CO_2 would warm the Earth by 3.6 °C. He also predicted that the concentration of CO_2 in the year 2000 would be 30% higher than in 1900, and that the average temperature of the planet would be 1 °C higher than a century earlier.

Despite these statements, Callendar, who had by then become a member of the Royal Meteorological Society and of the Glaciological Society in the United Kingdom, and Gilbert Plass found it difficult to convince the meteorological community of the importance of CO_2, and especially the *Met Office* in the United Kingdom. Many voices, especially in industrial circles, were strongly opposed to the idea that CO_2 could be responsible for global warming. Several of them disputed Callendar's analysis on the grounds that it was based on unreliable measurements. This was perhaps the starting point for the ongoing movement to question the influence of human activity on climate.

How could this controversy be resolved? The best method was to make systematic measurements of atmospheric carbon dioxide concentrations and infer their evolution over time. The International Geophysical Year in 1957-1958 provided an opportunity to propose a project for the long-term measurement of atmospheric CO_2.

Box 11.1. The Surprising Relationship between Atomic Physicists, Climate Specialists and the Military

In the aftermath of the Second World War, many of the nuclear physicists who had participated in the development of the American atomic bomb, notably at the secret center established at Los Alamos in New Mexico, turned their attention to new scientific questions: those relating to meteorology, oceanography, geology, air pollution and, more generally, climate. There were several reasons for this shift towards geophysical problems, some of which had a strategic and even military dimension[355].

[355] See in particular the article by Paul N. Edwards, Entangled histories: Climate science and nuclear weapons research, *Bulletin of the Atomic Scientists, 68*(4), 28-40, 2012.

The use of technology developed during the war, and in particular mass spectrometry developed as part of the Manhattan Project, enabled scientists who had been associated with the development of the atomic bomb including chemists Ernest Anderson (1920-2013), Harmon Greg (1926-2003) and James Arnold (1923-2012), to carry out isotope measurements in the environment to apply dating techniques[356]. Chemist Bernard Weinstock (1917-1981), who had been working on uranium enrichment, turned his attention to atmospheric smog issues in the 1960s after joining the Ford Motor Company. In 1955, Austrian physicist Hans Suess (1909-1993), who had been involved in the German nuclear energy project during the Second World War, joined the Scripps Institution of Oceanography in San Diego, California, where he carried out carbon isotope measurements to quantify the CO_2 budget in the atmosphere-ocean system.

It's interesting to note that several scientists directly involved in the atomic program were students or spent part of their professional careers at the University of Chicago. These included the geochemists Arnold, Greg and Anderson, as well as Edward Teller (1908-2003), a chemical engineer of Hungarian origin who emigrated to the USA in 1930, and Gilbert Plass (1920-2004), a physicist of Canadian origin who calculated the impact of CO_2 on the Earth's temperature. In Chicago, these atomic physicists benefited from an exceptional intellectual environment forged by prodigious scientists, some of whom won the Nobel Prize: Enrico Fermi (1901-1974), who built the first nuclear reactor; Harold Clayton Urey (1893-1981), who discovered deuterium and, with Stanley Miller (1930-2007), proposed a mechanism to explain the origin of life; Willard Frank Libby (1908-1980), who developed an isotope dating technique and whose work revolutionized archaeology and paleontology. In 1940, a meteorology department was set up at the same university, housing several renowned geophysicists and headed by Swedish meteorologist Carl-Gustaf Rossby. Between 1940 and 1945, more than 1,700 meteorologists were trained by this department to support the war effort.

Some of these scientists, noting that the world was entering an atomic age, were convinced that nuclear fission would provide the quantities of energy the planet needed to meet post-war economic challenges. As early as 1949, the U.S. Atomic Energy Commission asked an outside consultant, engineer Palmer Cosslet Putnam[357] (1900-1984), to carry out a general study on the likely energy demand over the next 50 to 100 years. In his 600-page report, published in 1953, Putnam addressed the problem of climate change, which at the time was still poorly appreciated and often ignored. He noted that:

> "Until very recently, at least, the weather has been getting warmer, especially in winter in northern latitudes. Glaciers are retreating. Sea level is rising because of glacial meltwater. There is a suspicion that man may have contributed to these effects by combustion and other habits.

[356] Cosmogenic isotope dating uses nuclides produced by cosmic rays to measure the length of time samples in the environment have been exposed to cosmic radiation. Carbon 14 (^{14}C), also known as radiocarbon, is one of the cosmogenic nuclides used.

[357] *Palmer Putnam*, a geologist who graduated from MIT in 1924, designed the first megawatt wind turbine in Vermont in 1941.

> [...] In the next 50 to 100 years we may burn up 10 times as much fuel as we have in the past 50 years. [...] Perhaps such a derangement of the CO_2 cycle would lead to an increase CO_2 content of the atmosphere great enough to affect the climate and cause a further rise of sea level. We do not know this. We ought to know it."

Six years later, in 1959, at a symposium organized by the American Petroleum Institute, the "father" of the hydrogen bomb, Edward Teller, tried to convince oil companies to turn to an alternative source of energy:

> "I am to talk to you about the energy of the future. [...] And this strangely, is the question of contaminating the atmosphere. [...] It has been calculated that a temperature rise corresponding to a 10 per cent increase in carbon dioxide will be sufficient to melt the icecap and submerge New York. All the coastal cities would be covered, and since a considerable percentage of the human race lives in coastal regions, I think that this chemical contamination is more serious than people believe."

An alumnus of the Universities of Karlsruhe, Munich, and Leipzig, Teller helped found the Lawrence Livermore Laboratory[358] in California, a public institute concerned with nuclear technology, energy, and the environment. Teller's mentor was Werner Heisenberg (1901-1976), head of the *Uranverein*, the German Third Reich's research program for industrial and military applications of nuclear fission.

One scientist played a major role in this transition from atomic physics to atmospheric science. At the end of the 1950s, mathematician Cecil "Chuck" Leith (1923-2016), a specialist in turbulence who contributed until 1946 to the program of the Oak Ridge nuclear center and then at the Lawrence Radiation Laboratory in Berkeley, established one of the first models of atmospheric general circulation at the Lawrence Livermore Laboratory, applying numerical methods developed by the physicists responsible for nuclear weapons development. In 1969, he joined the National Center for Atmospheric Research in Boulder, Colorado, to lead the climate modeling effort.

Scientists at the nuclear centers established high-performance numerical calculation methods for solving differential equations and processing large databases. The Livermore Center in California, the Los Alamos Center in New Mexico, the Oak Ridge Center in Tennessee, the Brookhaven Center in New York, and the Argonne Center in Illinois, now under the auspices of the US Department of Energy, all developed highly sophisticated climate models. All these centers had considerable computing resources available to both nuclear physicists and earth system modelers.

[358] The Lawrence Livermore National Laboratory (LLNL) was established in 1952, at the height of the Cold War, to advance nuclear weapons science and technology to meet national security needs. Scientists Ernest O. Lawrence (1901-1958) and Edward Teller (1908-2003) suggested the creation of a complementary laboratory at the Los Alamos Center to promote "new ideas" by adopting the multidisciplinary research approach developed by Lawrence, director of the *Radiation Laboratory* at the University of California, Berkeley.

Studying the impact of nuclear explosions on the atmosphere gave meteorologists a better understanding of the phenomena that determine the dispersion of radioactive substances in the air. This was emphasized by NOAA meteorologist Lester Machta (1919-2001) in an article with the unexpected title[359]: *The Meteorological Benefits from Nuclear Testing*. Machta, who had been hired by Harry Wexler (1911-1962) at the US Weather Bureau to work on special projects, showed that radioactive waste released during nuclear explosions was carried great distances in the atmosphere before falling back to earth. It posed a health hazard to populations around the globe.

In the 1950s and 1960s, the greenhouse effect provided a powerful argument for the increased use of nuclear energy. Similarly, the problem of fallout from radioactive particles released during nuclear explosions aroused fears among populations worldwide. So, it's no coincidence that, from this point onwards, funding for atmospheric and oceanographic research, along with nuclear physics, became priorities in the USA. Geophysicists, and particularly those developing the first mathematical models of the Earth system, benefited directly from the work carried out by atomic physicists, who had learned to solve the equations of hydrodynamics to simulate the shock waves produced in the atmosphere by nuclear explosions.

From the 1960s onwards, cooperation between the military and meteorologists expanded in several areas. An initial joint program between the Weather Bureau and the US Army, Navy, and Air Force focused on improving weather forecasting using numerical methods and the most powerful computers available at the time. This program was strongly encouraged by John von Neumann, who was also associated with the Manhattan Program. Secondly, the use of spacecraft to scan the Earth, its atmosphere, oceans, and continents by NASA and NOAA was of direct interest to the military. U.S. federal agencies also had access to "spy planes" that flew at high altitude to take air samples, which were analyzed in the laboratory and provided valuable information on the dispersion of radioactive debris in the atmosphere in the months following nuclear explosions. Finally, the military was interested in the atmospheric transport of dust grains raised during desert sandstorms. The reduced visibility caused by these natural phenomena is an obstacle to the proper operation of space-based remote sensing instruments. It also reduced the precision with which military aircraft bombarded desert regions during wartime.

A further question was raised in the 1970s as the Cold War intensified. The expected melting of polar ice as a result of climate change would enable the Soviets and Americans to deploy missiles in the more accessible areas of the Arctic. The opening of the Bering Strait in a world subject to global warming would also give military vessels easier access to waters close to American and Russian territories near the North Pole. Finally, for several years now, the military has been focusing on issues linking geostrategic challenges to climate change. In this spirit, the climate manipulation envisaged by some to limit global warming could enable states to achieve military objectives.

[359] Machta, Lester, Meteorological Benefits from Atmospheric nuclear tests, *Health Physics, 82*(5), 635-643, 2002.

The Keeling Curve

In 1954, under the impetus of Carl-Gustaf Rossby[360] (1898-1957), the first continuous measurements of atmospheric CO_2 concentration were initiated in Scandinavia. The Swedish-born American meteorologist, known for his studies of fluid mechanics and specifically large-scale atmospheric waves, had hoped to characterize the geographic origin of air masses travelling in response to meteorological disturbances. The relatively unsophisticated instruments of the time showed that carbon dioxide levels varied widely from one day to the next, ranging from 150 to 350 parts per million. Rossby believed that the variability that characterized the concentration of CO_2 would allow him to characterize the dynamics of the atmosphere. He therefore insisted that this chemical tracer be measured systematically at several points around the globe during the International Geophysical Year.

On the other side of the Atlantic, a young researcher hired as a post-doc by the California Institute of Technology (Caltech) in Pasadena, Charles David Keeling (1928-2005), measured the atmospheric concentration of CO_2 in a California state park where the *Big Sur* River flows down from the mountains

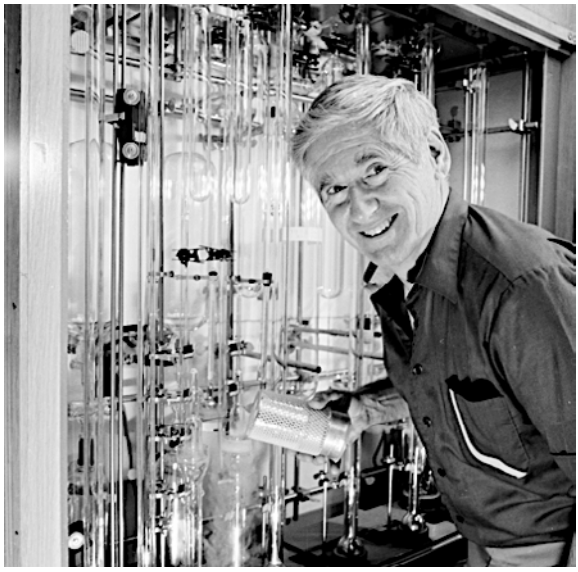


FIGURE 11.6: Charles David Keeling. © DR.

[360] Meteorologist Carl-Gustaf Arvid Rossby, a former student of Vilhelm Bjerkenes at the Institute of Geophysics in Bergen, Norway and at the University of Leipzig, became associate professor at MIT in Cambridge, MA in 1928 and professor at the University of Chicago in 1940. After the war years, during which he introduced several military personnel to meteorological concepts, he joined the Stockholm Institute of Meteorology and Hydrology in 1947, becoming its first director. After 1954, he contributed to the development of atmospheric chemistry, focusing on the effects of carbon dioxide on climate. He is particularly well known for his studies of large-scale wave propagation in the extratropical atmosphere.

into the Pacific Ocean. Contrary to what had been observed in Sweden, the CO_2 content of the air seemed to vary very little as a function of time; its value was always close to 310 ppmv. It was therefore necessary to clarify the reasons for this difference between the Rossby and Keeling measurements.

An interesting opportunity arose in 1956. At the instigation of Harry Wexler (1911-1962), the powerful director of research at the U.S. Weather Bureau, a measuring station was built at an altitude of almost 4,000 meters on the slopes of the *Mauna Loa* volcano overlooking the Big Island of Hawaii. This location, in the middle of the Pacific Ocean, was chosen to make measurements far away from industrial areas, in a region that was not disturbed by local emissions. Measurements taken at Mauna Loa were therefore representative of the background levels observed in the mid-latitudes of the Northern Hemisphere. Keeling convinced Wexler to install an instrument at the site to measure CO_2 continuously over several years. The goal was to test Callendar's theory that CO_2 levels in the air were increasing because of industrial development. Thanks to funding from the National Weather Service, four sophisticated air-analysis systems were purchased: one was installed on the Hawaiian volcano; a second was installed first at the *Little America* Antarctic station and then, a few months later, at the South Pole; a third was installed on a ship; and the fourth served as a reference system at the research laboratories of the Scripps Institution of Oceanography in La Jolla, near San Diego[361]. In August 1956, Keeling joined this facility, which was headed by the oceanographer Roger Randall Dougan Revelle (1909-1991). To detect a possible spatial variation in the concentration of CO_2 in the atmosphere, Revelle decided to make complementary measurements from instrumented aircraft.

Revelle left his mark on the American scientific landscape in the second half of the twentieth century. After receiving his Ph.D. from the University of California at Berkeley, he joined Scripps, where he focused on the role of the ocean in climate change. In addition to his remarkable scientific work, which made him an outstanding president of the American Association for the Advancement of Science (AAAS) in 1974, Revelle succeeded in convincing the U.S. Navy around 1950 to develop a major program of basic ocean research; at the same time, he was a brilliant advocate for the establishment of a University of California campus in San Diego. The campus was established in 1960. Revelle also defended ethical principles. During the era of McCarthyism, he protested the requirement that university professors take an anti-Communist oath, and a few years later, he opposed certain La Jolla residents who refused to rent or sell property in town to Jews.

The measurements of carbon dioxide from aircraft confirmed Keeling's views; the distribution of CO_2 in the atmosphere was relatively uniform over the mid-latitudes of the Northern Hemisphere, and the large variations recorded by Rossby's team were believed to be the result of measurement errors. However, initial measurements showed a seasonal variation of CO_2 in the atmosphere, with a maximum concentration in May and a minimum in October. This variation

[361] Established in 1907 with funding from newspaper magnate Edward Willis Scripps (1854-1924) and his half-sister Ellen Browing Scripps (1836-1932).

was attributed to carbon exchange between the atmosphere and the continental biosphere: in summer, plants grow by absorbing atmospheric CO_2, which is necessary for photosynthesis and the formation of organic matter; in winter, decomposing plant matter releases CO_2 into the atmosphere. This seasonal variation in atmospheric CO_2 was also present in airborne measurements but was of low intensity at the Little America station, which was far from vegetation-rich regions. In addition, the mean values measured at Mauna Loa were higher than those observed in Antarctica, highlighting the likely contribution of man-made emissions to the carbon cycle.



FIGURE 11.7: Mauna Loa Observatory, 3397 m above sea level on the Big Island of Hawaii © Mary Miller for NOAA.

Callendar had imagined that anthropogenic CO_2 had accumulated mainly in the atmosphere in the period following the Industrial Revolution, explaining the increase in its concentration in the air. This was not the view of Roger Revelle and his Scripps colleague Hans Eduard Suess (1909-1991). Suess was an Austrian-born nuclear physicist who received his Ph.D. from the University of Vienna in 1935 before moving to the University of Hamburg in 1938. During World War II, he was associated with the Third Reich's uranium project and collaborated with Norwegian researchers on the mechanisms of heavy water production. In 1950, Suess moved to the United States, where he first worked on cosmo-chemical problems at the University of Chicago before being recruited by Revelle at Scripps in 1955. There, he became interested in the exchange between the atmosphere and the ocean of a particular carbon isotope[362] carbon-14.

[362] Isotopes are used to distinguish two or more forms of the same chemical element whose nuclei contain an equal number of protons but a different number of neutrons; isotopes of the same element differ in atomic mass. The three isotopes of carbon are carbon-12 (the most abundant), -13 and -14.

Since the lifetime of this radioactive isotope is about 5,700 years, the density of carbon-14 in fossil material buried for millions of years is very low.

In 1957, Revelle and Suess noted that the isotopic ratio of carbon-14 to carbon-12 measured in tree trunks and marine animal shells had decreased slightly over the previous 50 years, suggesting that the presence of some of the carbon in the atmosphere and oceans was due to burned fossil fuels. They concluded from their measurements that, on average, a molecule of CO_2 from the combustion of these fossil fuels remains in the atmosphere for about 10 years before being dissolved in the ocean. They added[363]:

> "This means that most of the CO_2 released by artificial fuel combustion since the beginning of the industrial revolution must have been absorbed by the oceans. The increase of atmospheric CO_2 from this cause is at present small but may become significant during future decades if industrial fuel combustion continues to rise exponentially."

And:

> "Human beings are now carrying out a large-scale geophysical experiment of a kind that could not have happened in the past nor that could be reproduced in the future."

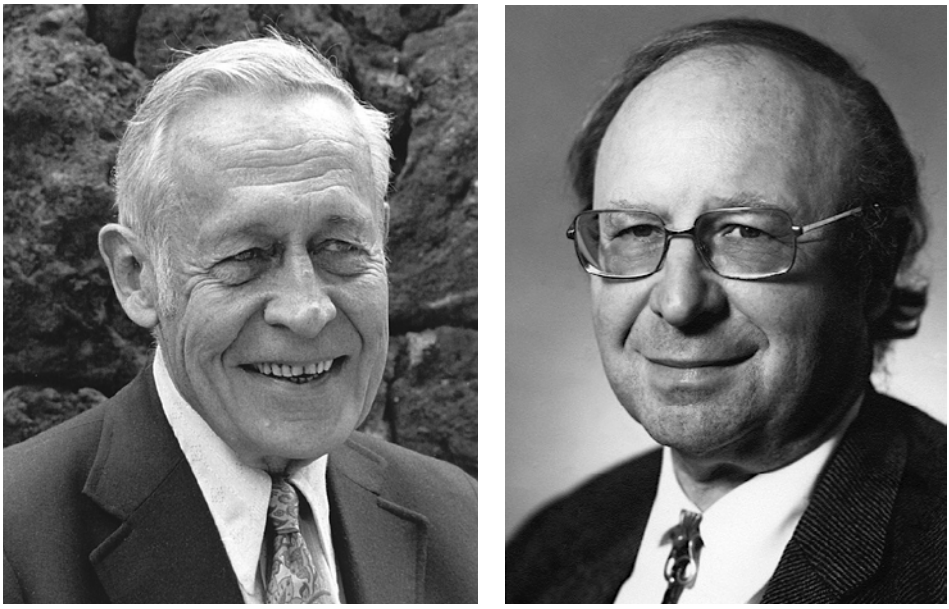


FIGURE 11.8: Roger Revelle and Hans Suess.

[363] Revelle, R., Suess, H.E. (1957). Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO_2 during the past decades. *Tellus, 9*(1), 18-27, https://doi.org/10.1111/j.2153-3490.1957.tb01849.x.

Finally, Revelle and Suess showed that physico-chemical processes in seawater buffer the uptake of CO_2 by the ocean. Consequently, only a fraction of carbon dioxide emitted in the atmosphere as a result of human activities is absorbed by the oceans. However, a question remained: was the average atmospheric concentration of CO_2 increasing over time, and was this increase consistent with the two Scripps researchers' estimate?

To answer this question, Keeling continued his CO_2 measurements at Mauna Loa despite the difficulties he faced in funding his research. The National Science Foundation, which strongly supported his initial efforts, stated that it was not allowed to fund routine observations. Nevertheless, the Department of Energy (DOE) and the National Oceanic and Atmospheric Administration (NOAA) continued to contribute. However, Keeling's program remained vulnerable to the vagaries of the budget situation and decisions made by U.S. agencies. In the end, the measurements continued without interruption. They clearly showed that the concentration of CO_2 in the atmosphere was continuously rising: the concentration of CO_2, which was around 315 ppmv in 1957 when measurements began, exceeded 400 ppmv in 2015. Keeling detected anomalies in the CO_2 measurements associated with the existence of periodic climatic variations, such as the 1971 El Niño phenomenon[364]. The role of continental vegetation and soils as sinks for atmospheric CO_2, in addition to that of the oceans, was also highlighted.

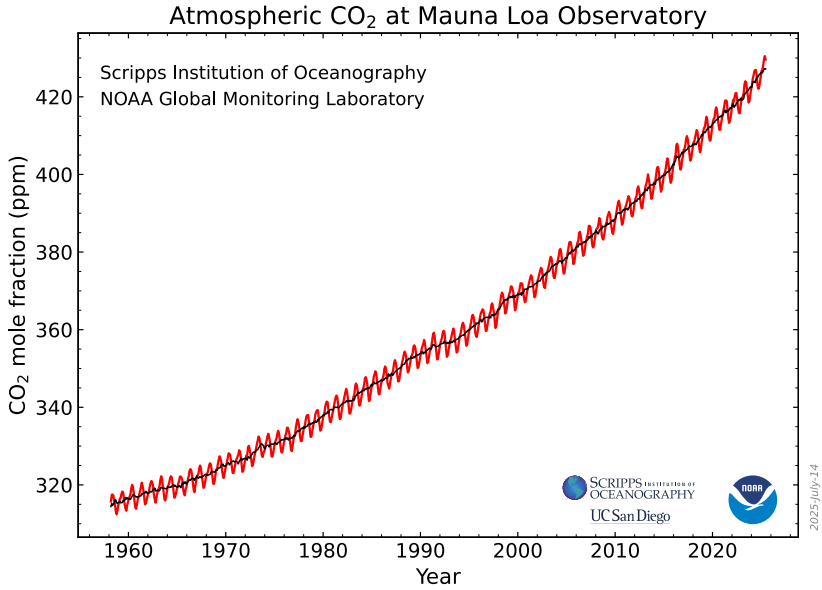


FIGURE 11.9: Evolution of the CO_2 concentration expressed in ppmv measured at the Mauna Loa Observatory station between 1957 and 2024.

[364] Global climatic phenomenon resulting from variations in sea surface temperatures in the tropical Pacific Ocean. The warming phase is known as El Niño and the cooling phase as La Niña.

The increase in atmospheric CO_2 revealed by Keeling's measurements prompted MIT to bring together climate specialists to prepare for the United Nations Conference on the Human Environment, to be held a year later in Stockholm. This "Earth Summit" proposed major measures to protect the planet. A group of thirty scientists from fourteen countries produced a document entitled "*Study of Man's Impact on Climate*" (SMIC)[365]. This report inventoried the major environmental problems facing the planet but failed to reach consensus on concrete actions to address the threat of climate change. The following year, the Stockholm Conference addressed issues such as water resources, desertification, the future of forests, aquatic life, and alternative energy sources, but climate change was not a central topic of discussion. Global warming was merely identified as a long-term risk.

Since the end of the nineteenth century, as atmospheric CO_2 levels have continued to rise, the planet has been gradually warming. An analysis of temperature measurements shows that between 1880 and 2010, the average temperature of the Earth's surface rose by nearly 0.8 °C. Between 1880 and 1910, the average temperature fell slightly, then rose until 1940. For the next forty years, it remained relatively constant before rising again significantly from the 1980s. In 2024, the globally averaged temperature exceeded the preindustrial value by more than 1.5 degree C.

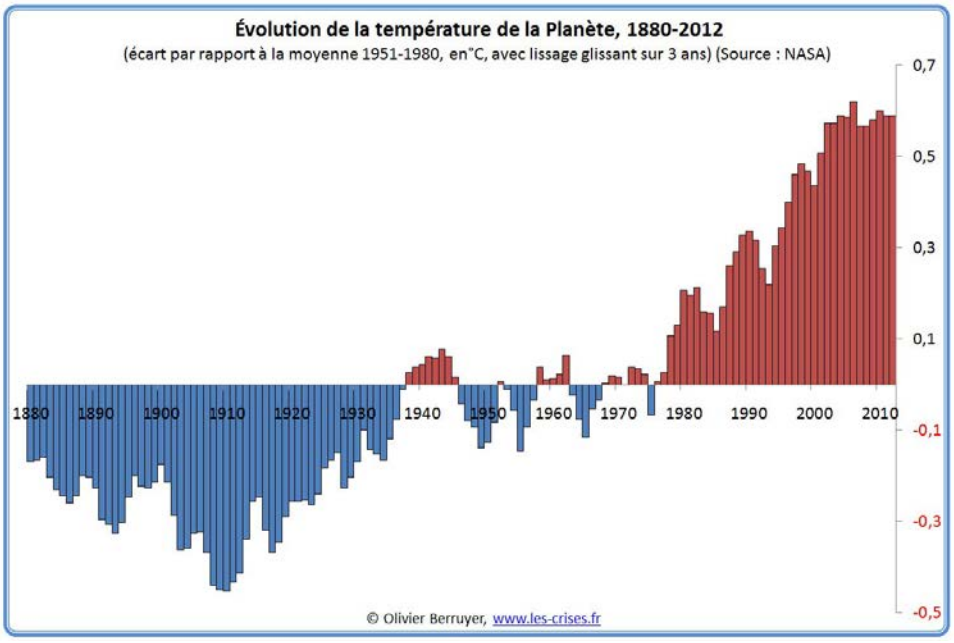


FIGURE 11.10: Deviation of the temperature between 1880 and 2010 relative to the 1951-1980 average value (global mean value). A sliding 3-year smoothing is applied to the measurements. © Olivier Berruyer.

[365] Inadvertent Climate Modification. *Report of the Study of Man's Impact on Climate (SMIC)*, MIT Press, Cambridge, MA, 308 pp., 1971.

Polar Ice: An Archive of Climate's History

At the beginning of the twentieth century, the question arose of how to obtain reliable information about past climatic variations. For the German geophysicist Alfred Wegener (1880-1930), author of the theory of continental drift, the ice that had accumulated in the polar regions over thousands of years should contain information about the history of the planetary system. In particular, the analysis of ice cores from Greenland or Antarctica should allow us to verify whether climate change is linked to cyclical variations in the Earth's orbital parameters[366] as proposed by the Danish-Norwegian geologist Jens Esmark (1763-1839), the English astronomer John Herschel (1792-1871), the Swiss biologist Louis Agassiz[367] (1807-1873), and the Scottish scientist James Croll (1821-1890). This hypothesis was taken up by Milutin Milanković (1879-1958) in his mathematical theory of climate[368]. This Serbian astronomer showed that the Earth should have experienced a succession of glacial (cold) and interglacial (warm) periods throughout history. Between 1919 and 1924, Milanković and his father-in-law, Russian-born climatologist Vladimir Petrovich Köppen (1846-1940), worked with Wegener to reconstruct past climate cycles.

In the late 1950s, an event occurred that would prove pivotal for climate research. Claude Lorius (1932-2023), then a student at the Université de Franche-Comté in Besançon, France, came across an interesting advertisement: the university was looking for students to take part in a polar expedition to mark the International Geophysical Year (1957/1958). The mountain enthusiast applied, and a few months later found himself in Terre d'Adélie[369] where he spent the winter at the scientific base named after Commandant Jean-Baptiste Charcot (1867-1936). This extraordinary experience opened up an amazing prospect for Lorius's research career: he would explore Antarctica by participating in several polar expeditions.

In 1965, a French team drilled into the ice cap of Terre d'Adélie. Lorius, who was part of the expedition, came up with a rather surprising hypothesis by examining the tiny air bubbles escaping from an ice cube he had put in his

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[366] Cycles of eccentricity (oscillation between a more elliptical and more circular form of the Earth's orbit) with a period of around 400,000 years for the main cycle and periods of around 100,000 years for the secondary cycles; cycle of obliquity (variation in the inclination of the Earth's axis of rotation) with a period of 41,000 years; cycle of precession of the equinoxes (variation in the orientation of the Earth's axis of rotation) with a period of 26,000 years.

[367] Jean Louis Rodolphe Agassiz, Swiss-born American biologist and geologist, is a specialist in the natural history of the Earth. After graduating from the Universities of Erlangen and Munich in Erlangen, he was appointed as the Professor of Natural History at the University of Neuchâtel. He emigrated to the United States in 1847 and became Professor of Zoology and Geology at Harvard.

[368] See Berger, A., Loutre, M.F., Théorie astronomique des paléoclimats, *Comptes Rendus Geoscience, 336*, 701-709, 2004.

[369] Coastal region of Antarctica south of Australia discovered in 1840 by French explorer Jules Dumont d'Urville (1790-1842).

whisky. He was convinced that this cube, taken from a core obtained during drilling, contained information about the chemical composition of the atmosphere at the time the ice formed. In this way, the analysis of ice cores should make it possible to reconstruct the climate of the past.



FIGURE 11.11: Claude Lorius (left) and Jean Jouzel (right).

In 1984, Lorius participated in another expedition, this time to the Vostok Antarctic base. Drilling carried out there by the Soviets since the 1970s reached a depth of 2,200 meters, giving access to ice that was 420 thousand years old. The ice cores were flown to France by American aircraft. They were analyzed by Lorius's team at the Grenoble Institute of Glaciology and by the group of paleoclimatologist Jean Jouzel at the École Polytechnique in Paris. The temperatures at which successive layers of ice formed were deduced from measurements of the oxygen isotope ratio ($^{16}O/^{18}O$) contained in frozen water molecules. The past evolution of atmospheric concentrations of carbon dioxide and methane was inferred from chemical analysis of the air trapped in the ice. These analyses confirmed the existence of natural climate cycles with successive periods of warming and cooling. Subsequent measurements at the Franco-Italian Concordia station, as part of the European EPICA project launched in 1995, made it possible to reconstruct the climate over a period of up to 800,000 years (eight glacial cycles). All these studies dramatically demonstrated that climate cycles run parallel to variations in the amount of carbon dioxide and methane in the air. Thus, there was a strong link between atmospheric concentrations of greenhouse gases and global surface temperature. By observing natural climate cycles, we can put current global warming trends into context and better understand the mechanisms that regulate the planet's climate.

Climate Models

Model formulation. At a conference on general circulation models held in Princeton in 1955, the American/Hungarian mathematician and physicist John von Neumann distinguished in his opening address three types of problems requiring the use of atmospheric models: First, short-term weather forecasting, which is highly dependent on the initial conditions of the problem and therefore requires a large number of observations characterizing the initial state of the atmosphere. The quality of forecasts can therefore be improved by multiplying the number of stations and other measurement platforms. Second, long-term simulations (of the climatic type), which are little affected by initial conditions but are influenced by boundary conditions, i.e., external "forcings" such as solar energy input or CO_2 emissions. Finally, medium-term predictions require knowledge of both initial and boundary conditions. This is the most difficult problem to solve and still represents today a real challenge for climatologists. See Box 11.2.

von Neumann's words led meteorologists to turn their attention to questions about the long-term evolution of atmospheric circulation. In principle, the prediction models mentioned in Chapter 4 provide information on the evolution of the main climatic variables. However, to deal with long-term trends, atmospheric models must be coupled with oceanic models because climate evolution is directly linked to the exchange of energy, carbon, and water between the different components of the planet. The three-dimensional formulation of the atmospheric and oceanic circulations makes it possible to simulate the transport of energy between geographical regions benefiting from a surplus of solar energy (the tropics) and those characterized by a deficit of this energy (the polar regions). The aim of the modelers is to calculate the evolution of average weather conditions over periods of several decades, in particular temperature, wind speed, and precipitation at any point on the Earth.

It was the meteorologist Norman A. Phillips[370] (1923-2019) who, in 1956, used an atmospheric circulation model for the first time to simulate the evolution of key climate variables, particularly their seasonal trends, over long periods of time. Phillips' computing resources at *the Institute for Advanced Study* (IAS) in Princeton were limited, so his model had only two atmospheric layers and was based on simplified equations (known as *quasi-geostrophic equations*).

In 1959, Joseph Smagorinsky, head of the Princeton group, invited Syukuro "Suki" Manabe, who had just completed his Ph.D. at the University of Tokyo, to join the Princeton team to further develop atmospheric circulation models. In 1965, the two scientists implemented a hemispheric model with nine vertical levels, using the so-called *primitive equations* rather than the simplified equations used by Phillips to describe air flows. Two years later, together with

[370] Phillips, N.A., The general circulation of the atmosphere: A numerical experiment. *Quarterly Journal of the Royal Meteorological Society, 82*(352), 123-164, 1956, https://doi.org/10.1002/qj.49708235202.

meteorologist Richard T. Wetherwald, Manabe determined the response of the climate system to a doubling of atmospheric CO_2. In a famous article[371], the two researchers estimated that the average global warming of the planet would be on the order of 2 °C.

In 1961, Smagorinsky hired oceanographer Kirk Bryan to develop an ocean circulation model. In 1969, Manabe and Bryan implemented a coupled atmosphere-ocean model[372] and demonstrated the importance of oceanic and atmospheric heat transport from low to high latitudes. In 1975, Manabe and Wetherwald showed that the warming at the Earth's surface due to a doubling of the amount of CO_2 in the atmosphere would be 2 °C in the tropical regions and more than 5 °C in the polar regions. Further, the stratosphere would cool by several degrees, reaching minus 5 °C at 30 km altitude. For his pioneering work in climate modeling, Manabe was awarded the 2021 Nobel Prize in Physics.

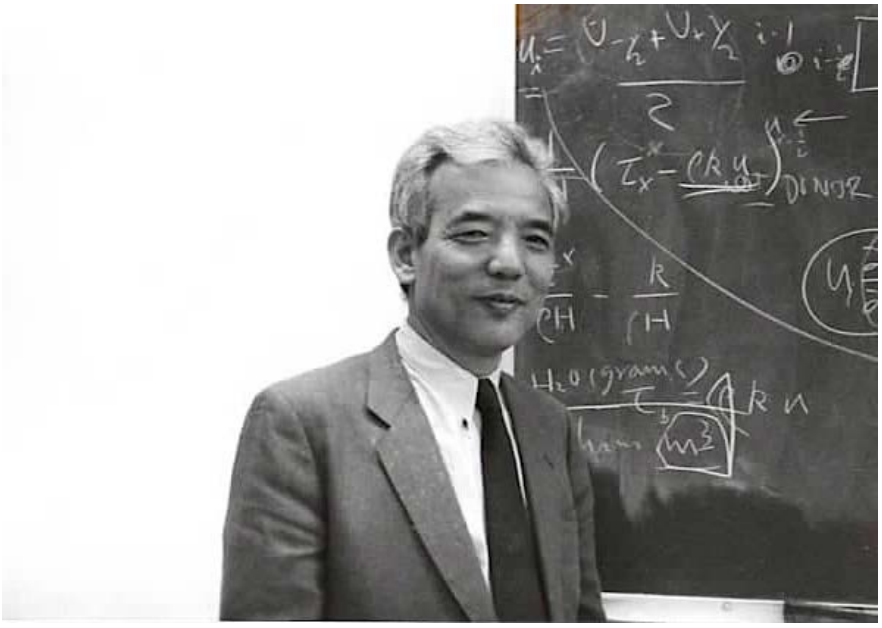


FIGURE 11.12: Syukuro Manabe. ©Suki Manabe.

[371] Manabe, S., Wetherwald, R.T., Thermal equilibrium of the atmosphere with a given distribution of relative humidity. *Journal of the Atmospheric Sciences 24*(3), 241-259, 1967.

[372] Manabe, S., Bryan, K., Climate calculations with a combined Ocean-atmosphere model. *Journal of the Atmospheric Sciences*, 786–789, 1969, https://doi.org/10.1175/1520-0469(1969)026<0786:CCWACO>2.0.CO;2.



FIGURE 11.13: Oceanographer Kirk Bryan (left) and climatologist Syukuro Manabe talk to *Geophysical Fluid Dynamics Laboratory* (GFDL) director Joseph Smagorinsky (right) in 1969. Source: Photo courtesy of the Geophysical Fluid Dynamics Laboratory.

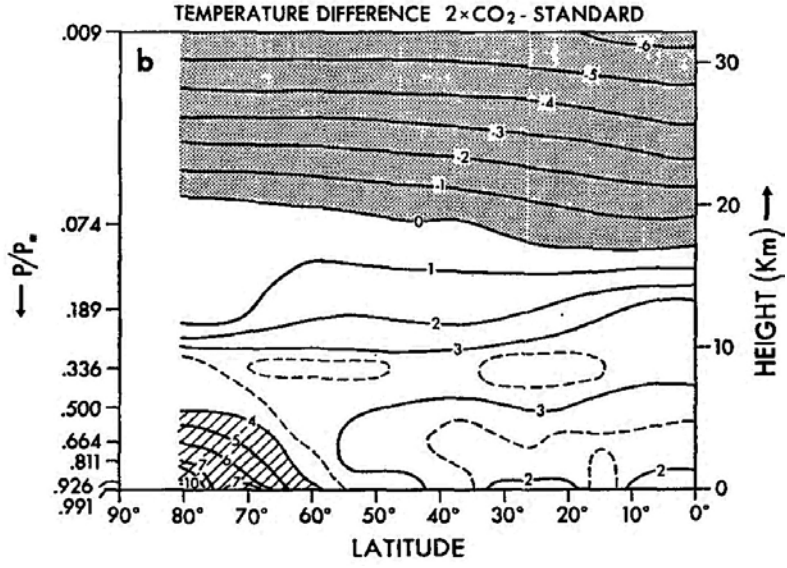


FIGURE 11.14: Difference in air temperature as a function of latitude and altitude resulting from a doubling of atmospheric CO_2 concentration. Values calculated in 1975 by Manabe and Wetherald using a three-dimensional climate model. Note the warming of the troposphere (2 to 3 degrees) and the cooling of the stratosphere, which reaches 5 degrees at 30 km altitude. Source: Manabe, S., and Wetherald, R.T., The Effects of Doubling the CO_2 Concentration on the Climate of a General Circulation Model. *J. Atmos. Sci.* 32(1), 3-15, 1975.

Other groups, especially in the United States, decided to develop their own models. This was the case at the University of California, Los Angeles (UCLA), where meteorologist Yale Mintz (1916-1991), a pioneer in atmospheric general circulation modeling, hired in the early 1960s a meteorologist from the University of Tokyo to contribute to this development. His name was Akio Arakawa (1927-2021). The global model resulting from this collaboration, the first version of which was released in 1963, included two atmospheric layers and took topography into account. The horizontal resolution was 7 by 9 degrees.

At NCAR in Boulder, Colorado, Akira Kasahara (1927-2022), who, like Manabe and Arakawa was educated at the University of Tokyo, worked with Warren Washington (1936-2024). Kasahara was associated with the Smagorinsky's



FIGURE 11.15: Four pioneers of climate modeling. Above, from left to right: Norman Phillips, Akio Arakawa. Below, from left to right: Joseph Smagorinsky and Klaus Hasselmann.

team and worked at Texas A&M University and the University of Chicago. Washington, originally from Oregon, received his Ph.D. from Pennsylvania State University and was a member of the National Academy of Engineering. In 1963, these two pioneers in climate modeling created a spectral model based on a method developed by the Australian Centre for Research into Numerical Methods in Meteorology[373]. In the following decades, NCAR continued to develop community models of the Earth system that are freely available to users worldwide.



FIGURE 11.16: Left: Akira Kasahara in the computer room at the National Center for Atmospheric Research in Boulder, Colorado. Right: Warren Washington receiving the National Medal of Science by U.S. President Barack Obama. Source: © University Corporation for Atmospheric Research (UCAR).

These early studies were a source of inspiration for many climatologists who, in the years that followed, began to develop increasingly complex and realistic models. Several institutions played an important role in the design and implementation of these models: in the United Kingdom, the UK Meteorological Office[374] and in Germany, the Max Planck Institute for Meteorology (MPI-M) in Hamburg. Klaus Hasselmann, director of the Hamburg research center until 1999, developed a stochastic climate model in the 1970s. He showed why models that simulate climate evolution are reliable even though atmospheric and oceanic dynamics are chaotic. For this work, he shared the 2021 Nobel Prize in Physics with Syukuro Manabe.

[373] Australian Numerical Meteorological Research Center.
[374] UK Meteorological Office (UKMO).

Box 11.2. Numerical Methods in Climate Models

The equations describing atmospheric and oceanic circulation do not have analytical solutions. To solve them, we have to turn to numerical methods that provide approximate solutions close to the real solution. Two types of methods can be distinguished: those with a local character (finite-difference, finite-volume, and finite-element methods) and those with a global character (spectral methods).

In the finite-difference method, proposed as far back as the eighteenth century by the English mathematician Brook Taylor (1685-1731) in his 1715 book *Methodus Incrementorum Directa and Inversa*, the continuous space characterizing the field of study is replaced by a mesh, and an approximate solution of the model equations is sought on the points of the corresponding numerical grid and for finite time intervals. Partial derivatives in space and time are replaced by analogous finite-difference expressions. Each differential equation is then replaced by an algebraic system of equations solved using a suitable numerical method. The choice of this method largely determines the execution speed of the calculation program. The solution of the system is thus obtained at a finite number of grid points and for specific time intervals. The distance between digital grid points provides a measure of the model's spatial resolution, and the time step a measure of the model's temporal resolution. These two factors determine the size and frequency of the physical and dynamic phenomena that can be explicitly represented by the model.

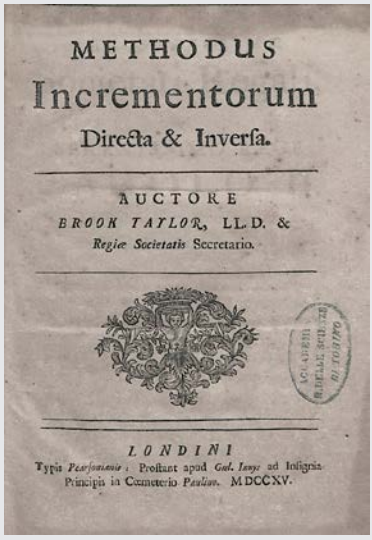

METHODUS
Incrementorum
Directa & Inverſa.
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BROOK TAYLOR, LL.D. &
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FIGURE 11.17: Book by Brook Taylor, introducing the finite-difference method in 1715.

The finite volume method exploits an integral form of the equations. The physical quantities sought are expressed as averages over small volumes adjacent to each other, known as grid cells. Solving the equations yields physical quantities averaged over these control volumes. In this method, the mesh can be unstructured and thus adapted to particular geometries or problems requiring a finer description of phenomena in part of the study domain.

In the spectral methods developed by S. A. Orszag and E. Eliasen in the early 1970s, the horizontal distribution of atmospheric variables is expressed by the superposition of a finite number of periodic functions. The coefficients providing the amplitude of the various harmonics vary with time and altitude; they are obtained by solving a system of ordinary differential equations whose independent variable is time. The number of waves used to express the physical quantities sought in the zonal and meridional directions constitutes

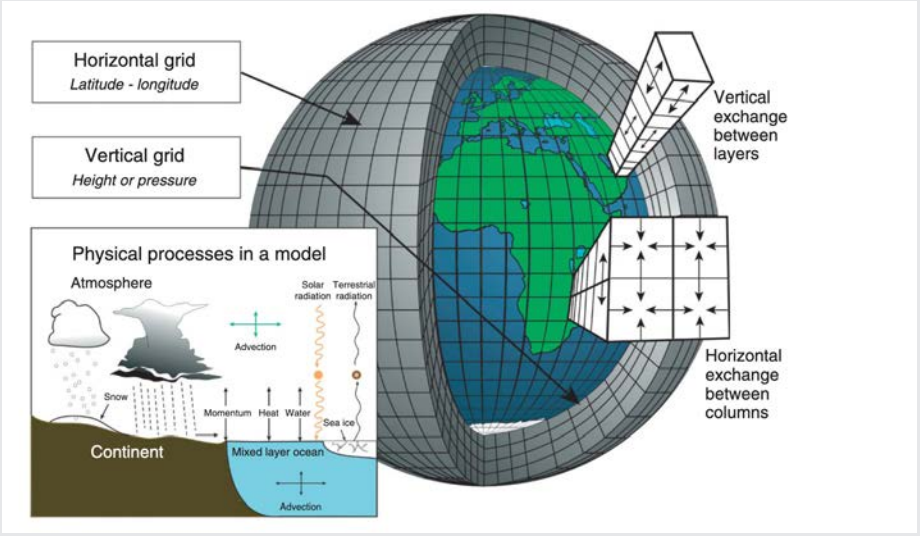


FIGURE 11.18: Schematic representation of a Cartesian grid used for the finite-difference solution of partial differential equations specific to climate models. The physical processes shown in the figure, which involve "subgrid" phenomena and therefore cannot be solved explicitly, are accounted for in the models by empirical formulations. Source: Edwards P.N., History of climate modeling. *WIREs Clim. Chang.,* 2, 128-139 (2011).

the truncation of the problem. The greater the number of harmonics, the higher the spatial resolution of the solution.

The local and global methods have each their advantages and disadvantages. Spectral methods, which were very popular in the 1980s, have been progressively abandoned in favor of local methods more suited to the architecture of modern electronic computers.

Finally, it should be stressed that small-scale processes such as surface-atmosphere exchanges, convective motions, cloud and precipitation formation, and ocean eddy formation cannot be represented explicitly in models with limited spatial resolution; their effects on the general circulation are taken into account by empirical or semi-empirical relationships based, for example, on experimental data.

Over the past few decades, the climate modeling community has focused its efforts on increasing the spatial resolution (horizontal and vertical) of models to improve the representation of medium-scale dynamical processes. Improvements have also been made in the formulation of physical processes whose characteristic size is smaller than the model resolution and which therefore need to be "parameterized". An adequate simulation of climate evolution must also consider the interactions that occur within the Earth system or between its components. These interactions can give rise to mechanisms that amplify or attenuate the

initial perturbations caused, for example, by human activities. These are called positive and negative feedback, respectively; they act simultaneously and constitute what the Ephesian philosopher Heraclitus (6^{th}-5^{th} century BCE) called "the harmony of opposing tensions"[375]. One positive feedback is the role of water vapor. As the Earth warms due to the release of CO_2, the evaporation of water from the oceans, and therefore, the amount of water vapor present in the atmosphere increases. Since water vapor is a very potent greenhouse gas, this leads to a significant amplification of global warming.

Climate models account for many possible feedback mechanisms, although their quantitative importance is not always well established. Feedback in the Earth system may include not only interactions between different physical processes that characterize climate, but also they often involves biological and chemical processes. To address this type of problem and to gain a broader understanding of the phenomena associated with climate change, additional modules have been progressively added to Earth system models. These modules simulate, for example, changes in the continental surface and may include a formulation that accounts for vegetation dynamics. Other modules represent CO_2 exchange mechanisms between the atmosphere, ocean, and continental biosphere. The mechanisms that characterize aerosol formation and chemical transformations of reactive species are also included in most current climate models.

The development of such models and the validation of their results can no longer be entrusted to a few isolated researchers in a particular laboratory, as was the case in the 1960s and 1970s. On the contrary, true multidisciplinary teams are now being formed, often requiring collaboration between different research institutions and international cooperation.

Climate computing. The advances in climate modeling have been made possible by the development of the most powerful electronic computers (Box 11.3). The speed at which computer programs can be executed has increased steadily over time, thanks to the rapid development of electronic components and architectures designed by the manufacturers of these machines. A computer's performance is generally measured in terms of the number of arithmetic operations it can perform in one second. The unit is called *flops*, an acronym borrowed from the expression *floating point operations per second*. This refers to the average performance, not the maximum performance of computers[376].

The rapid evolution of computing resources since World War II can be traced. The electronic computer built at the University of Manchester in 1947 performed about 200 operations per second (200 flops). The electronic components of this machine, like those of ENIAC, the first computer used in the United States to forecast meteorological trends, operated with electronic tubes (vacuum tubes) whose reliability was limited. The speed of the American

[375] Heraclitus, a pre-Socratic philosopher, believed that human beings evolve in response to an ensemble of opposing forces.

[376] Most of the values given here are borrowed from Michel Deville's book (Fluide numérique, Presses polytechniques et universitaires romandes, 2019) and relate to the specific case of solving the Poisson equation.

machine was about 400 flops, but breakdowns were frequent, delaying the execution of calculations. Climate research, however, benefited greatly from a new electronic component developed in 1947 by three physicists and engineers at Bell Laboratories in Murray Hill, New Jersey: William Bradford Shockley (1910-1989), John Bardeen (1908-1991), and Walter Houser Brattain (1902-1987), who were awarded the 1956 Nobel Prize in Physics: the transistor. Semiconductor technology was quickly exploited by a team at Manchester University, who built the first all-transistor computer in 1953. This machine was much faster and more reliable than its predecessors.

How could computer users communicate with these machines? An important innovation was introduced in 1953 by an employee of the International Business Machine Corporation (IBM), John Backus (1924-2007), who introduced a programming language known as FORTRAN (Formula Translator). This language, well-suited to intensive computing, was used for several decades to write computer codes for climate models. This universal and durable choice allowed different modeling teams to exchange codes between institutions and countries. The most modern versions of FORTRAN are still in use today, although other programming languages such as C, developed by the Americans Dennis Ritchie, Brian W. Kernighan and Ken Thompson at Bell Laboratories in the early 1970s, and its extension, the C++ language developed by the Dane Bjarne Stroustrup, also at Bell Laboratories, are gradually gaining ground[377]. The programming language Python, conceived in the late 1980s by Guido van Rossum at the Center for Mathematics and Informatics, replaces FORTAN in many applications. Interestingly, the name Python was inspired by the British surreal sketch comedy series *Monty Python's Flying Circus*.

Another prominent figure, the American engineer Seymour Roger Cray (1925-1996), made a remarkable contribution to the advancement of computer science, in particular to the development of supercomputers that allowed climate models to be run at much higher speeds than in the past. Cray began his professional career in Minnesota in 1950, when he joined Engineering Research Associates, a digital technology company that had grown out of a U.S. Navy laboratory specializing in building machines capable of breaking secret codes. However, he left this institution to help found a new company called Control Data Corporation (CDC), whose goal was to build the world's fastest computer. In 1964, Cray and his colleagues produced the CDC 6600 machine, considered to be the first commercial supercomputer. It produced 2 million flops (2 megaflops or 2×10^6 flops). Five years later, in 1969, the CDC 7600 produced 5 Mflops using integrated circuits.

In 1972, Seymour Cray left CDC to start his own company, the Cray Research Company, based in Minneapolis. In 1976, he produced a new type of supercomputer, the CRAY-1, which used vector data registers and computed at 50 Mflops (50×10^6 flops). The first prototype was loaned to Los Alamos National Laboratory for initial testing, but the first operational system was purchased by NCAR in Boulder, Colorado, for $8.8 million. This acquisition

[377] These programming languages are known as "*object-oriented*". They are based on the existence of classes and objects, as well as attributes and methods.



FIGURE 11.19: Seymour Cray next to the CRAY-1 supercomputer he designed and developed in 1976. The first machines, the most powerful in the world at the time, were used by the National Center for Atmospheric Research in Boulder, Colorado, and the Los Alamos (New Mexico) and Livermore (California) national laboratories. DR.

opened up new possibilities for the institution's climatologists and those at American universities, who were able to develop more advanced versions of their models. However, the computer codes had to be "vectorized"[378] to adapt to the new architecture of this machine. This innovation ushered in a new era of vector computing. Other, even more powerful supercomputers were marketed by the company. The most powerful of these machines produced several hundred Mflops. In Japan, NEC used the same vector architecture and produced the SX-5 in 1998, which achieved 8 gigaflops (8×10^9 flops) per processor. In 2003, the company built the 140-processor "*Earth Simulator*," which was the world's most powerful machine for two years, with a computing speed of 35 teraflops (35×10^{12} flops).

In the early 1990s, however, another architecture began to compete with vector machines. The most recent supercomputers used less expensive standard "Intel" processors rather than vector processors. The idea was to speed up the execution time of computer programs by parallelizing a very large number of processors. The era of *massively parallel* machines had just begun. Once

[378] A vector processor simultaneously applies the same processing to homologous elements of data arrays.



FIGURE 11.20: The *"Earth Simulator"* developed by the Japanese company NEC and installed in Yokohama in 2003 to run mathematical models of the Earth system. At the time, it was the most powerful computer in the world.

again, computer codes had to be modified to take advantage of this "parallelization". The first machines offered 1 teraflops of performance, but IBM's Blue Gene machines reached up to 15 teraflops in 2011. The race for more powerful machines continued, not only in the U.S., but also in Europe and Asia. The Tinanhe-2 machine built in China reached 61.4 petaflops (61.4×10^{15} flops) in 2013 and was the world's most powerful machine for some years.

Seymour Cray, who had always been skeptical of massively parallel computing, came up with an alternative solution that would allow him to regain control. In the early 1990s, he left his own company to found a new technology company, the Cray Computer Corporation, based in Colorado Springs. His goal was to build an ultra-fast scientific machine using new types of superconductors. The CRAY-3 he designed failed to catch on, however, and the company went bankrupt in 1995 for lack of bank credit; the only existing prototype was installed at NCAR. A year later, Seymour Cray, considered the founder of the supercomputer industry, died in a car accident in Colorado Springs.

Since the first successes attributed to scientific computer manufacturers, the race for computing power has continued unabated. The goal for the 2020s is to have supercomputers with an average execution speed of exaflops (10^{18} flops). The technological challenge is immense, as the increase in speed made possible by the relentless development of electronic components seems to have reached its limit. However, new technologies are promising. On the one hand, the use of *graphics processing units* (GPUs), which are particularly well-suited to intensive computing tasks, could at least partially replace traditional *central processing units* (CPUs). On the other hand, the use of optical technologies to replace semiconductors could be a major asset for HPC.

Box 11.3: Can Mathematical Models be Trusted?

In his book "*The Future of everything*", David Orrell writes: "Our impact on the planet can be visualized only with scientific technology that extends our senses to a global level. The important thing is that we do not allow an unbalanced and often fake insistence on objectivity to distance us from the world or cut off our connection to it. The future depends on the choices we make and the reactions of complex systems that are beyond our control. Decision-making in such situations relies as much on felt cultural and political values as it does on logical analysis. Objectivity and subjectivity must be in balance and inform each other, just like the positive and negative feedback loops that characterize living systems. We will choose to protect nature only if we value it, and not just as an object, but because it is alive. The only way we will respect it is if we understand that we cannot control it.

In non-linear complex systems, change often occurs abruptly, like water turning to ice. Extreme change is normal. It makes prediction difficult, but it also holds out tremendous hope, because it means that a sudden change in course can be expected. Such a change often comes from the bottom up, rather than from the top down; it comes as a felt reaction rather than something told to us by experts. Unlike deterministic mechanical systems, we have a choice; we can determine our own destiny. We are not slaves to the initial condition, our genes, or the efficient market. We are unpredictable, and that's no bad thing.

The science of complexity will not build a better global circulation model, nor will Gaia theory or Earth system science. Their stories are more of humility than of human ingenuity. But if we as a species are standing at a precipice, we should see the world feelingly than be completely blinded by our mental models; that know what we do not know. Creativity often emerges from a state of uncertainty. Grasping for illusory knowledge by over-modelling our environment is therefore part of the problem.

Even if we cannot predict storms, we can predict our ability to weather them. Engineers can calculate the vulnerability of structures to disasters such as flooding, hurricanes, and tsunamis, and help design suitable building codes. [...] But as our populations extend into floodplains and coastal areas, and global warming raises sea levels and increases the force of storms, we may find that the walls we built to withstand those once-in-a-lifetime storms are no longer high enough to keep the water out.

Mathematical models will always be indispensable. Like language, they are a way to understand the world, and organize and communicate our thoughts. They help us perform hypothetical experiments, explore possible scenarios, and expose fragilities. Most of all, they help us comprehend what is happening now. [...] Apollo's arrow cannot fly into the future or protect us from plague, but it may serve as a compass, point out dangers, and help us navigate an unpredictable world."

The Charney Report

By the end of the 1970s, all the studies conducted by the scientific community seemed to converge: the uninterrupted increase in atmospheric CO_2, well established thanks to Keeling's observations, seemed to pose an imminent threat to the planet. As early as June 1977, Frank Press (1924-2020), the director of the U.S. Office of Science and Technology Policy (OSTP), alerted President Jimmy Carter (1924-2924) to the possibility of future "catastrophic" climate change linked to fossil CO_2 emissions. In a memo to the president, he wrote

> "Because of the greenhouse effect of atmospheric CO_2, the increased concentration will induce a global climatic warming of anywhere from 0.5° to 5 °C. To place this in perspective, a temperature change of 5 °C would exceed in 60 years the normal temperature swing between an ice age and a warm period which takes place over tens of thousands of years."

Press enjoyed a high scientific reputation: The geophysicist had been a professor at Columbia University, the California Institute of Technology, and the Massachusetts Institute of Technology; in 1981, he became president of the National Academy of Sciences.

In 1979, the OSTP decided that it was time to take stock of what was known. This office at the White House had been created by Congress three years earlier to advise the President on the relationship between science and technology and their roles in national and international affairs. The Council asked the National Academy of Sciences to form a task force to provide an independent scientific assessment of the carbon dioxide and climate problem. The Academy appointed renowned meteorologist Jule Charney, professor at MIT, to chair the task force[379]. As a prelude to the Commission's work, the Chairman of the Academy's Climate Research Council, the Finnish-born American meteorologist Verner Edward Suomi[380] (1915-1995), professor at the University of Wisconsin in Madison, presented his views:

> "To address this question in its entirety, one would have to peer into the world of our grandchildren, the world of the twenty-first century. Between now and then, how much fuel will we burn, how many trees will we cut? How will the carbon thus released be distributed between earth, ocean and atmosphere? How would a changed climate affect the world society of a generation yet unborn?"

The working group met in July 1979 in Woods Hole, on the Atlantic coast south of Boston, and produced a report that was short (less than 20 pages) but clear and concise. It concluded that CO_2 levels were likely to double in the first half of the twenty-first century, resulting in equilibrium global warming of about

[379] The members of the working group are Akio Arakawa (UCLA), D. James Baker (U. of Washington), Bert Bolin (U. of Stockholm), Jule Charney (MIT), Richard M. Goody (Harvard University), Cecil Leith (NCAR), Henry M. Stommel (Woods Hole Oceanographic Institution) and Carl Wunch (MIT).

[380] Suomi is often considered the originator of space meteorology.

3 °C, with a probable error of ± 1.5 °C. The document noted the likelihood of more intense warming at high latitudes, but added that

> "Variations in these anomalies with latitude, longitude and season will be at least as great as the globally average changes themselves, and it would be misleading to predict regional climate changes on the basis of global or zonal averages alone."

The Charney Report, considered the first rigorous assessment of the climate issue, was hailed by the entire scientific community as a work based on scientific arguments and a sound understanding of the physical mechanisms specific to the atmosphere and the oceans. The document is still admired today: its conclusions, which are virtually identical to those of more recent studies, were presented at a time when the first signs of climate change were not yet apparent, and modeling tools were still very rudimentary. The working group's report also highlights the major uncertainties surrounding its assessments. One of these is the ocean's ability to absorb the heat generated by the greenhouse effect. If this heat transfer process is underestimated, the document says, warming could be less rapid than predicted. The report also highlights the uncertainties associated with physical feedbacks in the Earth system, including humidity and cloud cover.

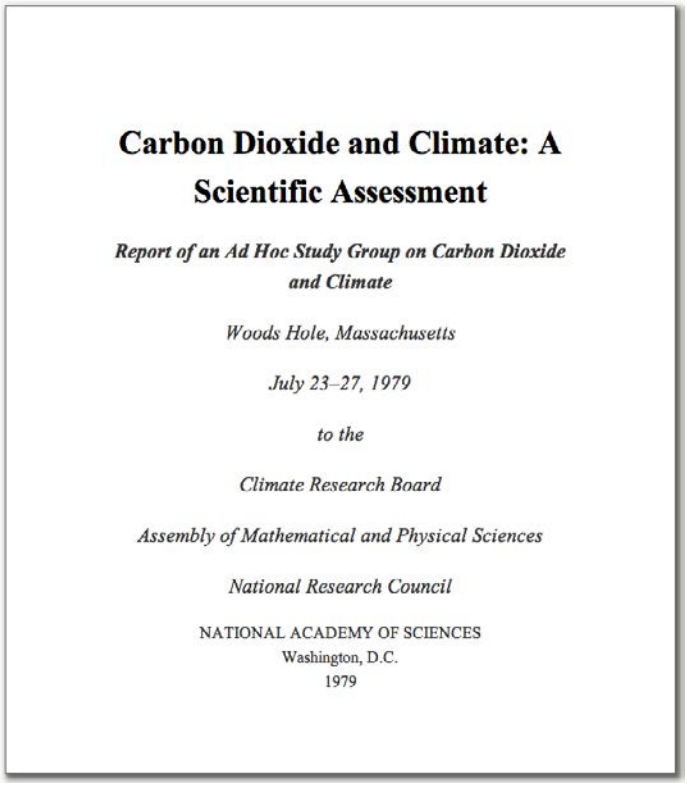


FIGURE 11.21: Cover page of the Charney Report (1979) considered to be the first scientific assessment of the climate problem. Source: National Academy of Sciences, Washington, DC.

Other scientific questions remained unanswered when the Charney Report was published. They became the subject of scientific studies in the following decades. They included changes in the reflectivity (albedo) of the land (desertification, melting ice, changes in the continental biosphere, etc.), the carbon cycle, natural emissions of methane and gases emitted by forest fires, interactions between clouds and the climate system, the role of fine particles in the radiative balance of the atmosphere, etc. Since the publication of the Charney Report, work has also focused on the absorption of anthropogenic carbon by the ocean and the continental biosphere. Finally, the response of dynamic processes to climate forcing, such as the tropical monsoon and El Niño phenomena, as well as possible changes in the intensity of ocean currents such as the Gulf Stream, received particular attention since the 1980s.

The Response of the Oil Industry

Despite the excellence of the scientific analysis that characterizes the document of the American Academy of Sciences, even if it did not address all aspects of the problem, the Charney report had limited impact in US political circles and was hardly known to the public. Only the oil industry became concerned about the alarming conclusions of this document, which blamed this economic sector for climate disruption and was thus damaging the commercial interests of the oil companies. Exxon, which knew about the potential consequences of CO_2 emissions since the 1950s, could no longer ignore this threat. It decided, therefore to conduct its own studies. A confidential technical report, intended for the company's senior management, showed the expected evolution of atmospheric CO_2 and average surface temperature over the next century. These projections were similar to those made by the academic community. Exxon's management, as well as that of other oil companies, were well aware of the climate changes looming on the horizon as a direct result of the burning of the fossil fuels they had produced and distributed around the world.

In response to the Charney Report, President Jimmy Carter asked the National Academy of Sciences to study climate change. A task force chaired by Nobel Prize-winning economist Thomas Schelling (1921-2016) highlighted the uncertainties in the science and called for more research rather than immediate action to limit CO_2 emissions. The U.S. government then asked the academy to conduct a more comprehensive study. This time, physicist William Aaron Nierenberg (1919-2000), director of Scripps", a prestigious research center on the Pacific Ocean in the pretty town of La Jolla, north of San Diego, California, was asked to chair the new task force. Nierenberg was a highly respected member of the Academy, having participated in the Manhattan Project during World War II. Members of the task force included such renowned climate specialists as Roger Revelle (University of California and Scripps), Joseph Smagorinsky (Princeton University), and Lester Machta (NOAA), as well as economists such as Thomas Schelling (Harvard University) and William Norhaus (Yale University). The very detailed study, published in

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M. B. GLASER
Manager
Environmental Affairs Programs

Cable: ENGREXXON, N.Y.

November 12, 1982

CO_2 "Greenhouse" Effect

82EAP 266

TO: See Distribution List Attached

Attached for your information and guidance is briefing material on the CO_2 "Greenhouse" Effect which is receiving increased attention in both the scientific and popular press as an emerging environmental issue. A brief summary is provided along with a more detailed technical review prepared by CPPD.

The material has been given wide circulation to Exxon management and is intended to familiarize Exxon personnel with the subject. It may be used as a basis for discussing the issue with outsiders as may be appropriate. However, it should be restricted to Exxon personnel and not distributed externally.

Very truly yours,

M. B. GLASER

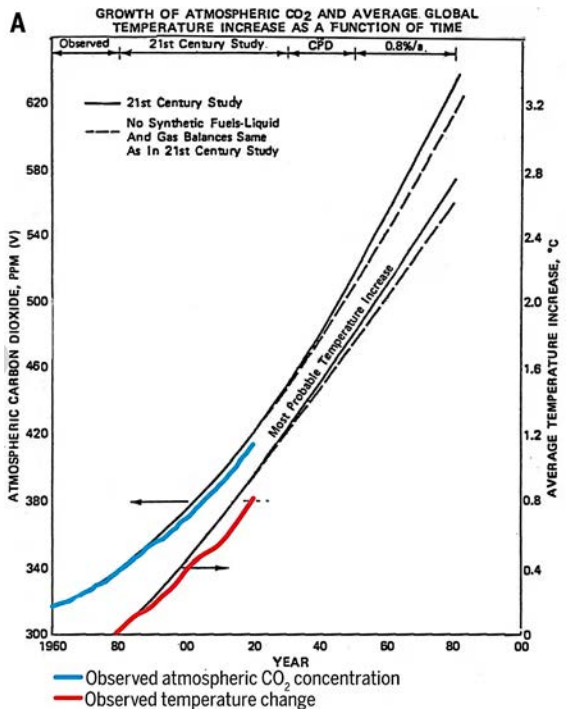


FIGURE 11.22: Top: Internal memo from M.B. Glaser, head of Exxon's environmental programs, dated November 12, 1982, on the greenhouse effect of CO_2. Bottom: graph extracted from this memo, showing the projections made by Exxon specialists, and in particular the projections of future CO_2 content (left-hand scale) and the resulting increase in the Earth's average temperature (right scale). In color, observed values very close to those projected by the oil industry.

October 1983[381] did not contain any significant new elements. It confirmed the conclusions of the Charney report but included several assertions that went beyond purely scientific considerations to include more political ones. The report called for further research but did not recommend measures to reduce the use of fossil fuels. For example, it stated:

> "We do not believe that the evidence at hand about CO_2-induced climate change would support to change current fuel-use patterns away from fossil fuels."

As Naomi Oreskes and Erik M. Conway wrote in their book entitled *Merchants of Doubt*[382]

> "Nierenberg's CO_2 and climate report pioneered all the major themes behind later efforts to block greenhouse gas regulation, save one. Nierenberg didn't deny the legitimacy of climate science. He simply ignored it in favor of the claims made by the economists: that treating symptoms rather than causes would be less expensive, that new technology would solve the problems that might appear so long as government didn't interfere, and that if technology couldn't solve all the problems, we could just migrate. In the two decades to come, these claims would be heard again and again."

In an article published in 2010[383] Nierenberg's son, Nicolas disputed the views of Oreskes and Conway, claiming that the report's scientific conclusions reflected the consensus at the time. Nor, he adds, have other reports called for changes in energy policy.

President Carter also asked the National Commission on Air Quality to propose policies to mitigate climate change. In response to this request, environmentalist Rafe Pomerance organized a meeting in October 1980 at the Don Cesar Hotel, an iconic pink building on the Gulf of Mexico in St. Petersburg, Florida. Inside this palace, scientists, environmentalists, U.S. policy experts, federal officials, and a member of the Exxon Corporation gathered. With these motivated participants, the development of a new energy strategy to address climate change was within reach. However, in the absence of real leadership from the U.S. government, participants were unable to agree on how to reduce oil production without damaging the economy. Hope, no doubt a bit utopian, gave way to disappointment. The conference was a failure; an extraordinary opportunity had been lost. Four days after the end of the conference, Ronald Reagan (1911-2004), elected president of the United States, promised to eliminate environmental regulations that he considered to be a brake on his country's economic development.

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[381] *Changing Climate: Report of the Carbon dioxide Assessment Committee*, National Academy Press, 1983.

[382] Oreskes, N., Conway, E.M., *Merchants of Doubts. How a Handful of Scientists Obscured the Truth on Issues from Tobacco Smoke to Global Warming*, Bloomsbury Press, New York, 355 pp., 2010.

[383] Nierenberg, N., Tschinkel, W.R., Tschinkel, V.J., Early climate change consensus at the National Academy: The origins and making of changing climate. *Historical Studies in the Natural Sciences*, 40(3), 318-349, 2010.

The oil companies then gradually withdrew from the climate debate, joining the automobile, mining, and electricity sectors in insisting on the uncertainties that characterize climate projections. They claimed that it was too early to take action that would limit greenhouse gas emissions. The *Global Climate Coalition*, founded in 1989 by several business groups, and the *George C. Marshall Institute,* a think tank founded in 1984 to promote conservative ideas on issues related to science, policy, and defense, and, in a second phase of its existence, to environmental issues and climate change. William Nierenberg, who chaired the Academy's 1983 report on CO_2 and climate change, was one of the founders of the Marshall Institute. These well-funded associations have challenged the major findings of the science and attempted, with some success, to sow doubt and thus reduce public confidence in climate scientists (Box 11.4).

As for the political leaders, they continued their consultations, especially through parliamentary hearings, which multiplied during the eighties. In March 1982, the young congressman from Tennessee, Al Gore, who had been taught by the legendary Roger Revelle, organized a parliamentary meeting on the greenhouse effect with the participation of James Hansen, director of NASA's Goddard Institute for Space Studies and professor at the Earth Institute of Columbia University in New York.

A few years later, invited to testify again, this time before the U.S. Senate Committee on Energy and Natural Resources, Hansen stated on June 23, 1988, that

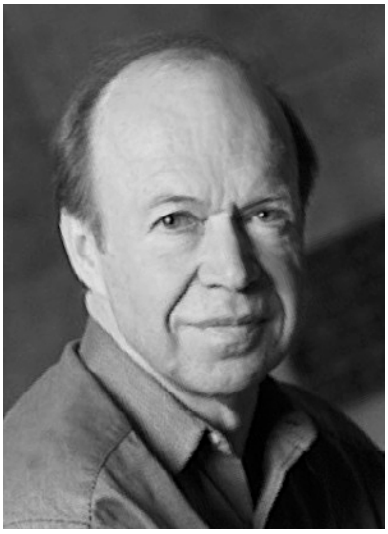
> "global warming has reached a level such that we can ascribe with a high degree of confidence a cause and effect relationship between the greenhouse effect and observed warming."

According to NASA experts, global warming was the result of the accumulation of greenhouse gases in the atmosphere, not a random fluctuation linked, for example to solar variability. Almost a year later, on May 9, 1989, Hansen was invited to another hearing, this time by the Senate Subcommittee on Transportation, chaired by Senator Al Gore. Appropriately, the NASA scientist submitted the text of his speech to government authorities in advance. To his great surprise, part of the text had completely disappeared in the document returned to him. He warned Al Gore, who alerted the press. The George H. W. Bush administration, through the White House Office of Management and Budget, censored the scientist's message, causing a wave of outrage and disapproval in the scientific community.

"They are scared of the truth."

declared Al Gore, who saw in this attitude the desire of the American executive to avoid the adoption of an international treaty on global warming.

An influential figure in the Bush administration was playing a controversial role in climate policy. John Henry Sununu, President George H.W. Bush's chief of staff from 1989 to 1991, was an MIT graduate and considered himself close to science and technology. The former Republican governor of New Hampshire was openly opposed to the introduction of CO_2 emission regulations, which he

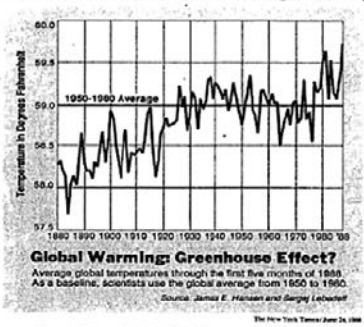


"All the News That's Fit to Print"

The New York Times

VOL.CXXXVII... No. 47,546 NEW YORK, FRIDAY, JUNE 24, 1988

Global Warming Has Begun, Expert Tells Senate



Global Warming: Greenhouse Effect?

Average global temperatures through the first five months of 1988. As a baseline, scientists use the global average from 1950 to 1980.

Source: James E. Hansen and Sergej Lebedeff

Sharp Cut in Burning of Fossil Fuels Is Urged to Battle Shift in Climate

By PHILIP SHABECOFF

Special to The New York Times

WASHINGTON, June 23 — The earth has been warmer in the first five months of this year than in any comparable period since measurements began 130 years ago, and the higher temperatures can now be attributed to a long-expected global warming trend linked to pollution, a space agency scientist reported today.

Until now, scientists have been cautious about attributing rising global temperatures of recent years to the predicted global warming caused by pollutants in the atmosphere, known as the "greenhouse effect." But today Dr. James E. Hansen of the National Aeronautics and Space Administration told a Congressional committee that it was 99 percent certain that the warming trend was not a natural variation but was caused by a buildup of carbon dioxide and other artificial gases in the atmosphere.

An Impact Lasting Centuries

Dr. Hansen, a leading expert on climate change, said in an interview that there was no "magic number" that showed when the greenhouse effect was actually starting to cause changes in climate and weather. But he added, "It is time to stop waffling so much and say that the evidence is pretty strong



Cañon Zapata in Tijuana, Mexico, the busiest illegal crossing point.

Drought Raising Food Prices; Inflation Effect Seems Minor

By ROBERT D. HERSHEY Jr.

Special to The New York Times

FIGURE 11.23: Above: James E. Jansen, director of NASA's Goddard Institute for Space Studies. Bottom: Front page article reprinting James E. Hansen's testimony during his June 23, 1988, congressional hearing. Source: New York Times.

believed would be detrimental to the development of the American economy. He procured a mathematical climate model and installed it on the computer in his White House office. This would allow him to "verify" the results of the numerical simulations carried out by the academic world. He was convinced, for example, that scientists significantly underestimated the absorption by the ocean of the heat produced by greenhouse gases.

In any case, as the 1980s drew to a close, the lobbies denying the role of greenhouse gases in climate change were gaining strength, with the financial backing of some industry and the active support of certain political leaders, particularly in the ranks of the American Republican Party. The conclusions of the Charney Report, widely accepted in the early 1980s, were being challenged by these politically motivated groups. The concept of climate change once again became a controversial "hypothesis". Figures that discredit climatologists were appearing in the media with increasing frequency. Some American researchers were even being questioned and their work strongly criticized by parliamentary and governmental bodies.

The International Dimension

In spite of the efforts by conservative groups to deny the reality of global warming, the problem of climate change soon took on an international dimension. At the first World Climate Conference, held in Geneva in February 1979 under the auspices of the World Meteorological Organization (WMO), the World Climate Research Programme (WCRP) was established. It aimed to determine the predictability of the climate and to assess the impact of human activities on it. In October 1985, a major meeting was held in Villach, Austria, jointly organized by the United Nations Environment Programme (UNEP), the World Meteorological Organization (WMO), and the International Council of Scientific Unions (now the International Council for Science (ICS)). The participants confirmed that the increase in atmospheric CO_2 will inexorably lead to a significant rise in the Earth's average surface temperature during the first half of the twenty-first century. But they went one step further: they established a group of experts[384] to actively address the impact of greenhouse gases under the name *Greenhouse Gas Advisory Group*. Discussions at the conference showed that it was essential to develop a mechanism for evaluating research results and communicating the resulting scientific information to decision-makers.

How could such a synthesis mechanism be established? And should this mechanism be the sole responsibility of scientists, to avoid pressure from outside groups? The Reagan administration, which was in power at the time, did not want to give scientists *carte blanche* to deal with what it considered a highly political issue. The issue was discussed in Toronto in June 1988 at a 300-person conference entitled *The Changing Atmosphere: Implications for Global Security* held three days after James Hansen's remarkable testimony before the U.S. Senate. Participants agreed that the climate threat was as serious as the nuclear threat and therefore a threat to international security. The conference recommended a reduction by 2005 in CO_2 emissions of about 20% below the 1988 levels. Following the conference, the World Meteorological Organization and the United Nations Environment Programme established

[384] The Advisory Group on Greenhouse gases, established under the aegis of WMO, UNEP and ICSU, began work in 1986.

the *Intergovernmental Panel on Climate Change* (IPCC), the successor to the Greenhouse Gas Advisory Panel.

The mission of the IPCC was to provide the world with a clear scientific picture of the current state of knowledge on climate change and its potential environmental and socio-economic impacts. This new institution would therefore provide detailed assessments of the state of scientific, technical, and socio-economic knowledge on climate change, its causes, potential impacts, and coping strategies, without conducting its own research. The IPCC became an intergovernmental group since government representatives were involved in setting the broad lines of the reports, appointing the authors, reviewing the reports, and accepting, adopting, and approving the reports in plenary sessions.

Bert Rickard Johannes Bolin (1925-2007), professor of meteorology at Stockholm University, became the chair of the IPCC. A former student of Carl-Gustav Rossby, Bolin worked with Jule Charney and John von Neumann at the Institute for Advanced Studies in Princeton in the 1950s, when the first attempts at computerized weather forecasting were made. Since the 1960s, Bolin had been interested in the carbon cycle in the Earth system and had been an advocate of genuine international cooperation on climate-related issues. But it was also his reputation as a brilliant and honest scientist who respected the sometimes-divergent opinions of different groups that made Bolin an excellent chairman of the IPCC from 1988 to 1997. Sir Robert Watson, his successor at the helm of this institution of several hundred scientists, said of Bolin[385]:

> "Bolin's quiet, soft-spoken style earned him the trust and respect not just of government officials who already recognized the threat of human-induced climate change, but also of those who vehemently challenged the idea that Earth's climate was even changing, let alone whether humans were involved. [...] Rarely does a single individual change the world, but Bolin's work as a scientist, as an organizer of major international research programs and as leader of the IPCC has certainly changed the way we think about the world. That we are now aware of the potentially catastrophic impact of human activities on Earth's climate, and of the need to make the transition to a low-carbon economy and to protect our natural forests, is in no small part down to him."

The IPCC produces an assessment report every five to six years. Three working groups took stock of scientific knowledge on climate change (Working Group I), assessed the socio-economic and environmental impacts of climate change (Working Group II), and formulated response strategies (Working Group III). The first report was published in 1990, and the conclusions were cautious and undoubtedly evasive:

> "If the order of magnitude of the [observed] warming is broadly consistent with the results of climate models, it may also correspond to natural climate variability, so that this could be largely responsible for the observed thermal

[385] *Nature, 451*, 642, 2008.

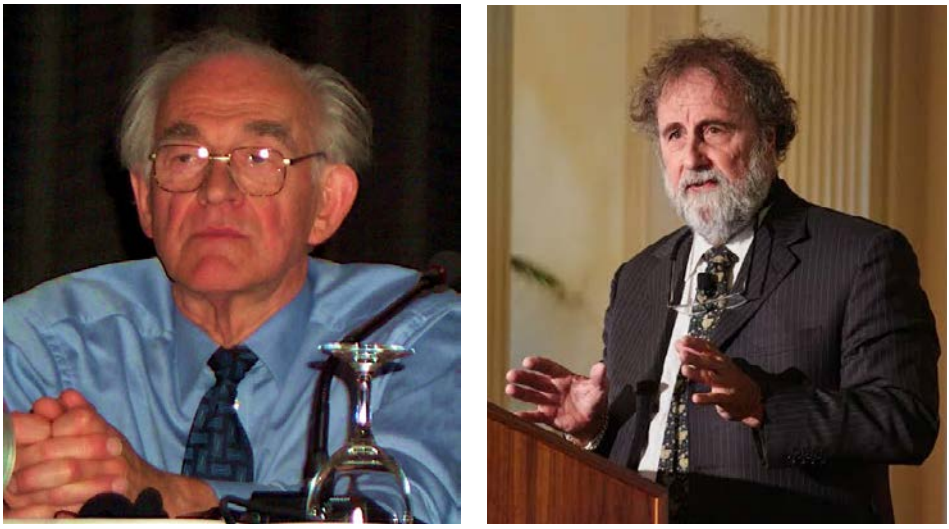


FIGURE 11.24: Bert Bolin and Sir Robert Watson, the first two chairmen of the IPCC.

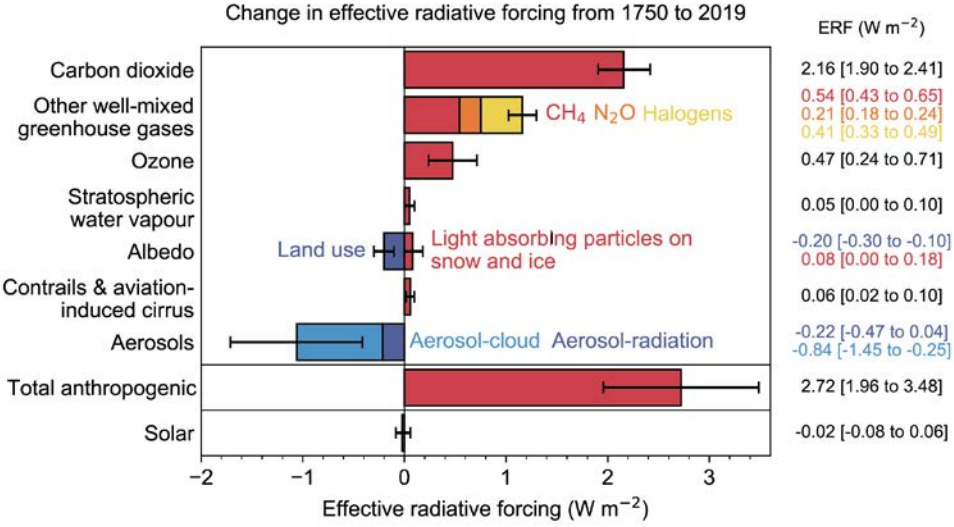
rise; on the other hand, this natural variability, combined with other anthropogenic factors, could have offset even more considerable warming due to a human-induced greenhouse effect."

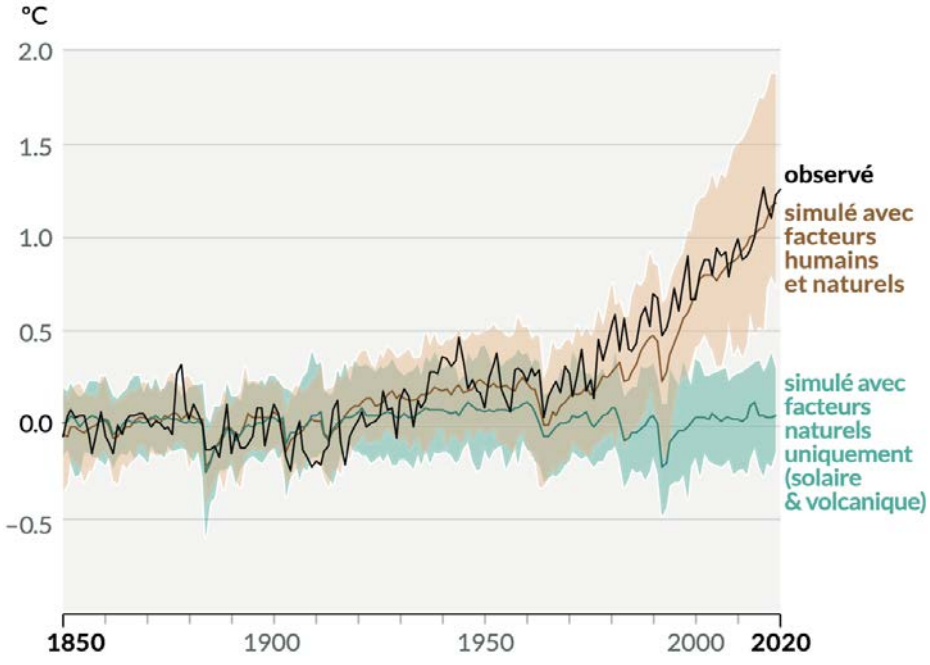
The second report, published in 1995, was more definitive, stating that "a body of evidence points to the existence of a discernible human influence on climate". The third and fourth reports, published in 2001 and 2007 respectively, stated that most of the global warming observed since the mid-twentieth century was likely (2001) or very likely (2007) to be the result of increasing greenhouse gas concentrations. The 2013/2014 and 2021/2022 reports reaffirmed this viewpoint by unequivocally attributing global warming to anthropogenic causes.

In 2000, Sir Robert Watson, Chair of the IPCC, put the findings of the IPCC's Third Assessment Report into perspective:

"The question is not whether climate will change in response to human activities, but rather how much (magnitude), how fast (the rate of change) and where (regional patterns). It is also clear that climate change will, in many parts of the world, adversely affect socio-economic sectors, including water resources, agriculture, forestry, fisheries and human settlements, ecological systems (particularly forests and coral reefs), and human health (particularly diseases spread by insects), with developing countries being the most vulnerable. The good news is, however, that the majority of experts believe that significant reductions in net greenhouse gas emissions are technically feasible due to an extensive array of technologies and policy measures in

the energy supply, energy demand and agricultural and forestry sectors. In addition, the projected adverse effects of climate change on socio-economic and ecological systems can, to some degree, be reduced through proactive adaptation measures."





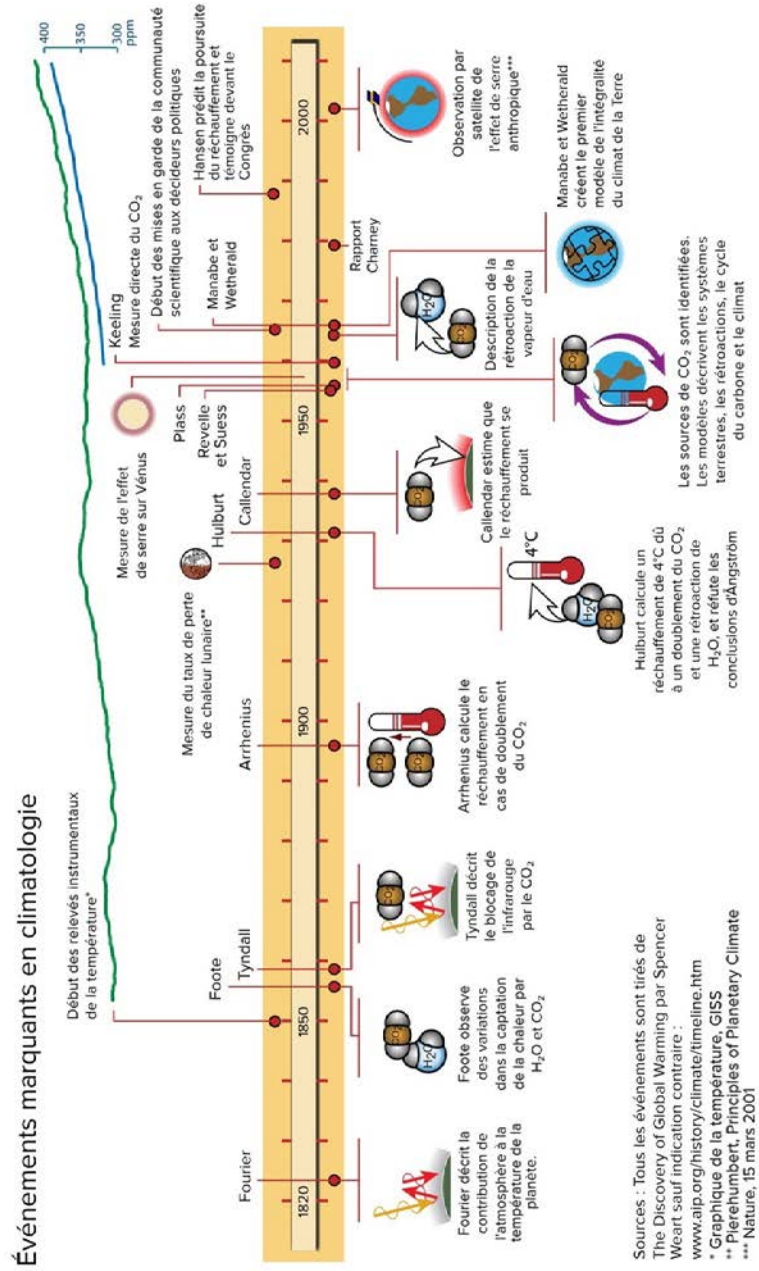


FIGURE 11.25: Some results from the 2021 IPCC report. Top (previous page): Radiative forcing between 1750 and 2019 due to estimated changes in CO_2, CH_4, N_2O, halogen compounds, ozone, stratospheric water vapor and surface albedo. The effects of aircraft contrails and the direct and indirect effects of aerosols are also shown. Middle (previous page): Evolution of the Earth's mean temperature between 1850 and 2020, observed and calculated considering only natural factors and natural and human factors. The colored area on either side of the two curves shows the scatter of the results obtained by the mathematical models. Bottom: Summary of the history of climate research.

Box 11.4. Climatoskepticism and Climatodenialism

The reports of the Intergovernmental Panel on Climate Change (IPCC) are intended to support the policy-making process by being "policy-relevant but not policy-prescriptive". In reality, the IPCC does not conduct its own research; it merely synthesizes and analyzes the work of the international scientific community as a whole. The panel's conclusions are reviewed by a wide range of experts and government officials, and the report's authors respond in writing to each of the thousands of comments received during the review process. Synthesis documents for decision-makers are reviewed - word for word - and approved by government delegates representing all countries participating in the IPCC effort. All IPCC-published documents are public.

However, despite the consensus that had developed within the research community, since the 1980s a small number of scientists, often with prestigious backgrounds, claimed that the research lacked objectivity and that the conclusions of the IPCC reports were biased and often incorrect. For these individuals, these documents should not have been considered by decision-makers. Many of these deniers belonged to the generation of scientists strongly influenced by the economic role of the two superpowers of the time. Their actions were often supported by a few foundations, notably the *George C. Marshall* and *Heartland Institutes*, two conservative American think tanks focusing on science and policy, and the *Global Climate Coalition*, an international corporate lobby group that questioned the science behind climate change. Their work was encouraged and even funded by several multinational corporations.

In their book "*Merchants of Doubt*", Oreskes and Conway[386] highlight the motivations behind this strategy. Deniers, supported by politically committed think tanks and, in some cases, industry and banking groups, have consistently opposed measures to protect the environment, including acid rain reduction, climate protection, and even limiting tobacco consumption. The authors conclude that the motivation is essentially ideological. They add:

> "Why did this group of "cold warriors" turn against the science to which they had previously devoted their lives? Because they felt [...] that they were working to 'maintain the benefits of freedom'. If science was used against those blessings - in a way that challenged freedom of enterprise - then they would fight it as they would fight any enemy. Indeed, science was beginning to show that certain kinds of freedom are not sustainable - like the freedom to pollute. Science was showing that Isaiah Berlin[387] was right: freedom for wolves does indeed mean death for lambs."

[386] Oreskes N. and Conway E. M., Merchants of Doubt: How a Handful of Scientists Obscured the Truth on Issues from Tobacco Smoke to Global Warming, Bloomsburry, 2010.

[387] Sir Isaiah Berlin (1909-1997) was a Russian-British social and political theorist, philosopher and historian of ideas.

Some also saw in the attitude of the negationists an intellectual dishonesty that hides behind a pseudo-expert facade. In an article published by *Le Monde*, William Audureau[388] writes:

> "Dismantling the climato-skeptic argument is a Sisyphean task. It corresponds to Brandolini's law, well known to observers of the world of disinformation, according to which proving the absurdity of a spiel proves far more costly in time and energy than producing it. [...] Unlike the sophism cited by Freud, anti-scientific rhetoric is neither witticism nor dream logic. On the contrary, it underscores a very conscious effort to undermine scientific consensus by every possible means."

And he added that the climate-skeptic public has changed in recent years:

> "It's no longer about experts on the bangs, but about citizens steeped in distrust, conspiracists, antivaxers and Putinolaters."

The Political Process and Climate Agreements

Twenty years after the first conference on the human environment, held in Stockholm in 1972, the United Nations Conference on Environment and Development, more commonly known as the *Earth Summit*, was held in Rio de Janeiro, Brazil, from June 3-14, 1994. One hundred and seventy-nine countries were represented by political leaders, diplomats, senior officials, scientists, and representatives of non-governmental organizations. The results were substantial: three conventions were adopted, one on climate change, a second on the protection of biological diversity, and a third on the principles of forest management. A major outcome of the conference was the adoption of an ambitious program, called *Agenda 21*, aimed at implementing new investment strategies to achieve sustainable development in the twenty-first century.

In the wake of the Earth Summit, the *United Nations Framework Convention on Climate Change* (UNFCCC) was established in 1994 with the goal of stabilizing greenhouse gas concentrations at a level that would prevent disruption of the climate system. Each year, the *Conference of the Parties* (COP) meets to develop concrete climate action. In 1997, at the third Conference of the Parties (COP3) in Kyoto, Japan, a protocol was adopted to reduce between 2008 and 2012 the global emissions of six greenhouse gases (CO_2, methane, nitrous oxide and three organic chlorinated compounds) by 5% relative to 1990 levels. To enter into force, the *Kyoto Protocol* had to be ratified by a number of countries whose total emissions represented at least 55% of 1990 CO_2 emissions. The agreement signed by the United States has never been ratified by Congress. It wasn't until 2004 that Russia ratified the Protocol, reaching the 55% target. This latter ratification allowed the Protocol to enter into force on February 16,

[388] Audureau William, Le climatosceptisme, anatomie d'une mauvaise foi, *Le Monde*, May 29, 2023.

2005. Canada, which originally ratified the treaty, decided in December 2011 to officially withdraw from it. In the words of Canadian Prime Minister Stephen Harper, "Kyoto is essentially a socialist plot to extort money from the richest countries".

On December 12, 2015, the 21st Conference of the Parties (COP21) in Paris adopted an international treaty aimed at limiting warming "to well below 2 degrees Celsius" and continuing efforts "to limit the temperature increase to 1.5 degrees Celsius above pre-industrial levels". The *Paris Agreement*, adopted by 196 parties, is a milestone in the multilateral climate change process. For the first time, it is an agreement that commits all nations determined to combat climate change and adapt to its impacts. The agreement entered into force on November 4, 2016. However, the United States withdrew from the protocol twice, each time under the Republican Trump administration: once in 2019 (with a decision effective November 4, 2020, but the Biden administration rejoined the agreement on January 20, 2021) and a second time in January 2025.

Solutions to the Climate Problem

At the beginning of the twenty-first century, climate change appears to be becoming a reality from which our societies cannot escape. Mathematical model projections show that climate change, which is already being felt today, will become much more severe by the 2040s. In the face of this disruption, finding solutions will require the efforts of governments and businesses around the world, as well as the efforts of each and every citizen. This is an unprecedented challenge for humanity.

In an article published in *Le Monde* on September 25, 2023[389], a group of climatologists, physicists, chemists, biologists, geophysicists, agronomists, economists, lawyers, and political scientists call for a global mobilization to face an unprecedented challenge:

> "At a time when one climatic disaster follows another - fires, floods, heatwaves, droughts - it is now undeniable that global warming poses an existential threat. Limiting this warming and adapting to it is an imperative and overriding duty: the greatest challenge in human history. In agriculture, industry and transport, fossil fuels form the very basis of modern industrial society. Doing without them implies a new collective organization, and in particular a profound transformation of our technical and industrial tools. Decarbonizing the energy, physical, chemical and agricultural processes that underpin the industrialized world in order to avoid millions of deaths: this is our historic responsibility."

Mitigating climate change. To limit the extent of climate change, we must make a rapid transition to decarbonized energy sources, whether solar, wind, hydroelectric, or nuclear. This means fundamentally transforming industrial

[389] "French scientists call for a Manhattan Project of ecological transition", *Le Monde* September 25, 2023.

production systems, modes of transportation, and agricultural practices to achieve sustainable development in our economic systems. *Mitigating* climate change is our first challenge, a challenge that is directed to those responsible for greenhouse gas emissions and climate disturbances.

Adapting to climate change. At the same time, in order to limit the impact of the climate disruptions that will undoubtedly become unavoidable, we need to invest in infrastructure to protect people, such as new flood barriers, dikes to protect against rising sea levels, agricultural practices adapted to the droughts expected in certain regions, improved building insulation, and urban planning to better protect people from extreme weather events. In the spirit of environmental justice, we must also protect the most vulnerable populations, for example, by providing them with financial protection to cope with the disasters that could affect them. *Adaptation* to climate change is our second challenge, a challenge addressed this time to society as a whole.

Manipulating the climate. Ultimately, in the absence of sufficiently ambitious action to limit climate change, we may one day need to undertake large-scale interventions to protect populations and ecosystems. The idea of modifying weather and climate conditions is not new. At the end of the nineteenth century, when Arrhenius concluded from his work that the onset of a new ice age could be avoided by burning the carbon buried in mines, he was already thinking about a means of manipulating the climate. Meteorologists, however, were the first to attempt to disrupt the atmosphere, initially on a local or regional scale.

As early as 1841, in his book *The Philosophy of Storms*[390], American meteorologist James Espy, whose work we mentioned in Chapter 4, wanted to provoke rain by burning vast areas of forest. For Espy, who saw the atmosphere as a gigantic heat engine, the energy provided by deliberate forest fires would create convective air currents that would transport water vapor to the upper, colder layers of the atmosphere, where it would condense and produce precipitation. Other mechanisms have been suggested. During the American Civil War, for example, rain was reported to have been caused by artillery fire; in the 1870s, some imagined that rain could be caused by explosions[391].

However, it was not until 1932, following research conducted in Leningrad, that the Soviets attempted to produce rainy episodes by seeding clouds with calcium chloride particles from airplanes. In the US, in 1946, engineer Irving Langmuir (1881-1957), winner of the 1932 Nobel Prize in Chemistry, and his colleague, meteorologist Vincent Schaefer (1906-1993), proposed introducing silver iodide and ice crystals into clouds containing supercooled water droplets. This technique, still controversial today, is still practiced in several countries, notably China.

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[390] Espy, J.P., *The Philosophy of Storms*, Charles C. Little and James Brown, Boston, 1841.

[391] See Fleming, J.R., The pathological history of weather and climate modification: Three cycles of promise and hype. *Historical Studies in the Physical and Biological Sciences*, 37(1), 3-25, 2006.

For some political leaders, the manipulation of weather and climate was a new way to manage their territory and strengthen their country's economy. This was the thinking of Joseph Stalin (1878-1953), who developed his *Great Plan for the Transformation of Nature* in 1948. In 1961, at the 22nd Congress of the Communist Party of the Soviet Union, the USSR's scientific community was urged to give priority to the study of how to manipulate weather situations. As for military strategists, they believed that deliberate weather and climate modification could be a highly effective weapon of war. The possibility of provoking floods, diverting hurricanes, or creating droughts became a national security issue and part of the Cold War problem. In fact, in 1957, Henry Garrett Houghton (1905-1987), chairman of the meteorology department at MIT, stated:

> "I shudder to think of the consequences of a prior Russian discovery of a feasible method for weather control. Fortunately for us and the world we were first to develop nuclear weapons [...] International control of weather modification will be as essential to the safety of the world as control of nuclear energy is now. [...] Basic research in meteorology can be justified solely on the economic importance of improved weather forecasting but the possibility of weather control makes it mandatory."

During the 1960s, work on these issues developed rapidly in both antagonistic blocs but stalled a decade later. On the one hand, attempts to produce rain proved ineffective and thus no longer of much interest to the military; on the other hand, the nascent environmental movement spoke out against the practice. Nevertheless, in the late 1960s, during the Vietnam War, the Americans tried to produce heavy rain to limit the movement of Viet Cong fighters along the Ho Chi Minh Trail. France had already used such methods at Diên Biên Phu in 1954.

The idea of manipulating atmospheric conditions not locally but on a planetary scale, and thus controlling global warming, began to gain ground in the 1950s. As early as 1955, John von Neumann, in an essay entitled *Can We Survive Technology*[392]? wrote:

> "Let's now consider a completely "abnormal" industry and its potential - that is, an industry that doesn't yet belong on any list of major activities: weather control or, to use a more ambitious and justified term, climate control. [...] All meteorological phenomena, as well as the climate as such, are ultimately controlled by the solar energy that falls on the earth. Changing the amount of solar energy is, of course, beyond human capabilities. But what really counts is not the quantity that hits the earth, but the fraction retained by the earth [...]. Now, the quantity absorbed by solid earth, the sea or the atmosphere seems to be subject to delicate influences. It is true that none of these elements has so far been really controlled by human will, but there are strong indications of possible control. [...]

[392] "*Can We Survive Technology*?", John von Neumann Collected Works, ed. A. Taub, Vol. VI, pp. 504-519.

> Microscopic layers of colored matter distributed over an icy surface or in the atmosphere above such a surface could inhibit the process of radiation reflection, melt the ice and alter the local climate. The measures that would achieve such changes are technically feasible, and the amount of investment required would only be of the order of magnitude required to develop rail systems and other major industries."

Three years later, in 1958, Harry Wexler, head of research at the U.S. *Weather Bureau*, retorted in *Science* magazine that proposals to modify the weather on a large scale were "either impractical or likely to produce cures that are worse than the ailment". In 1965, however, a report by US President Lyndon Johnson's (1908-1973) *Science Advisory Committee* raised the possibility of modifying the Earth's albedo, without any reference to the need to reduce CO_2 emissions. The concept of climate control, or *geoengineering*[393] to use a term introduced by the Italian physicist Caesare Marchetti (1927-2023), had supporters such as John von Neumann and the father of the hydrogen bomb, Edward Teller (1908-2003), who was the director of the Lawrence Livermore National Laboratory[394].

In 1994, Russian climatologist Mikhail Ivanovich Budyko (1920-2001) proposed offsetting the global warming that occurred between 1920 and 1940 by injecting some 200,000 tons of sulfur into the stratosphere. Once converted into aerosols, these molecules would reflect a significant portion of the sun's incoming radiation back into space. The idea was to artificially reproduce the effects of a powerful volcanic eruption. Budyko added in his book entitled *Climatic Changes*[395]:

> "These climate modification measures are intended to prevent or mitigate climate changes that could occur in several decades' time as a result of man's economic activity. However, such modification is not beyond the reach of modern technology. In the near future, it will apparently be possible to modify the climate, [...] producing a drop in global temperature of several degrees."

The idea was taken up again in 2006 by Paul Crutzen[396] who proposed to study the climate effects of injecting fine particles into the stratosphere. His work brought the issue of climate manipulation to the forefront of public debate and provoked sometimes violent reactions. However, Crutzen was not calling for the implementation of such a solution; he was merely asking that its potential effects be studied. This would be a last-chance solution, to be adopted only if other approaches failed. He believed that scientists needed to quantify

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[393] See, Royal Society, *Geoengineering the Climate: Science, Governance and Uncertainty*, Royal Society, London, GB, 98 pp., 2009; Keith, D.W., Geoengineering the climate: History and prospect. *Annual Review of Energy and the Environment 25,* 245-84, 2000; Caldeira, K., Bala, G., Reflecting on 50 years of geoengineering research, *Earth's Future, 5*, 10-17, 2017.

[394] Marchetti, C., On geoengineering and the CO_2 problem, Climate Change, 1, 59-68, 1977.

[395] Budyko, M.I., *Climatic Changes*, American Geophysical Union, 1077.

[396] Crutzen, P., Albedo enhancement by stratospheric sulfur injection: A contribution to resolve a policy dilemma, *Climatic Change, 77*, 211-220, 2006.

the impact of such measures. Modifying the reflective properties of clouds and deploying giant space mirrors above the Earth were also being considered, as they would also allow *solar radiation management* in the atmosphere.

Another method, known as *carbon sequestration*, was proposed and studied by industry: this involved eliminating the excess CO_2 present in the atmosphere by reforestation, fertilizing the oceans, or implementing industrial processes to store this gas in deep layers of the Earth.

Climate manipulation raises significant scientific, political, and ethical issues. First, there is the possibility of unforeseen environmental impacts, including harmful regional imbalances. For example, a report on solar radiation management prepared by a group of experts for the European Commission in 2024 showed that none of the technologies proposed to reduce the amount of solar energy captured by the Earth system, including injecting particles into the stratosphere and increasing the albedo of clouds, is currently a mature technology. Further, this solution in no way solves the problem of ocean acidification caused by CO_2.

Second, in the absence of an international regulatory framework to implement such a project, certain countries or private players could unilaterally launch geo-engineering actions that would lead to geopolitical tensions and perhaps conflict between states.

Finally, and most fundamentally, human manipulation of the climate system runs counter to the desire to respect nature and live in harmony with it. Is it, as climatologist Valérie Masson-Delmotte points out, a folly of sorcerers' apprentices[397]? And, as Marine de Guglielmo Weber[398] asserts, isn't this a desire to change the planet's atmosphere rather than changing our way of life? The anthropocentric vision of the "climate engineers" implies a domination of technology over nature and thus calls into question a respectful and harmonious relationship with the environment. And as James R. Fleming notes[399]:

> "By emphasizing the purely technical aspects of strategies of weather and climate control, bypassing understanding and prediction, and neglecting the historical, ethical and social dimensions, we are in danger of entering a new cycle of discourse saturated with hype, the heirs of an impoverished debate."

In any case, by the early 2020s, a growing number of scientists believe that the implementation of techniques to voluntarily modify the climate will become inevitable, even if the consequences of such undertakings are not fully known. Others believe that research in this area must continue in order to inform policymakers about the benefits and risks of such measures. But, as Eric Lambin, a professor at the Catholic University of Louvain, points out, "beware the slippery slope" between research and implementation!

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[397] See the paper by Audrey Garric in *Le Monde* of 26 January 2025 under the title: "Face à l'utilisation "inéluctable" de la géo-ingénierie solaire, des scientifiques appellent à une gouvernance mondiale".

[398] Marine de Gugliemo Weber, researcher at the Institute for Strategic Research at the *École Militaire* in France and author of the book together with Rémi Noyon, *Le grand retournement*, Les Liens qui Libèrent Publisher, 2024.

[399] Fleming J. R., op. cit.

The Complexity of the Earth System

In the last decades of the twentieth century, scientists realized that the study of the "Earth System" could not be limited to the climatic processes mentioned above. In fact, the Earth evolves not only under the influence of physical processes but is also subject to biogeochemical cycles and economic and social phenomena. All of these interact on scales of time and space that can be highly variable.

The concept of the Earth as a complex dynamic system subject to interactive processes has a long history. As early as the 18th century, one of the fathers of modern geology, James Hutton (1726-1797), who believed that the Earth's distant past could be studied by examining sedimentary rocks, asserted that the Earth is a *superorganism* that should be the subject of physiological studies in the same way as living organisms. In 1857, the Austrian geologist Eduard Suess (1831-1914) introduced the concept of the *biosphere*. It soon became clear that the *Earth system* was not only subject to natural forcing processes such as solar energy and volcanism, but also increasingly to the effects of human activity. As early as 1864, this led the American philologist George Perkins Marsh (1801-1882) to publish a book entitled *Man and Nature, or Physical Geography Modified by Human Actions*. This Republican diplomat is often considered the first American ecologist to recognize the irreversible impact of human activity on our planet. A few years later, in 1873, the Italian Catholic priest Antonio Stoppani (1824-1891) described the geological epoch ushered in by the dawn of the industrial age as the *Anthropozoic era*.

In Russia, Vladimir Ivanovich Vernadsky (1863-1945) was interested in the evolution of the Earth. Born to a Ukrainian father and Russian mother, Vernadsky was an exceptional mind and is sometimes considered the father of Soviet science. He studied geochemistry, mineralogy, physics, and biology at St. Petersburg University, then traveled to Europe to continue his studies in Naples, Munich, and Paris. Returning to Russia in 1902, he was appointed a professor at Moscow University but resigned in 1911 to protest the tsar's repression of students who had attended the funeral of the writer Leo Nikolayevich Tolstoy (1828-1910). In the early 1900s, the geochemist entered politics and helped found the Democratic Constitutional Party, of which he remained a member until 1918. In 1908, he was elected to the Russian Academy of Sciences.

In opposition to the Bolsheviks[400] who had seized power in Russia, the geochemist left Russia and fled to Ukraine. There, he founded the Ukrainian Academy of Sciences, whose members were encouraged to feel close to Russian culture. The country, then in the hands of German occupiers, was soon rocked by

[400] Bolshevism is a revolutionary Marxist movement whose origins go back to the Second Congress of the Russian Social-Democratic Workers' Party. This congress took place in 1903, initially in Brussels, but was later forced to move to London. Lenin's radical tendency prevailed over Martov's more moderate one. In October 1971, the Bolsheviks took power in the soviets (councils of workers, peasants, and soldiers in the Russian Empire that had taken power in certain local organizations) and refused to share that power with other political parties.

public unrest, persecution, and uprisings before coming under Communist control. Vernadsky moved to Crimea, where he taught mineralogy before becoming director of the university in 1920. However, he returned to Russia just as the Red Army seized Crimea.

Beginning in 1922, Vernadsky was invited by the rector of the Sorbonne to spend three years in Paris. It was in this city, where he gave a series of seminars, that he met two Catholic thinkers, the French mathematician and philosopher Edouard Le Roy (1870-1954) and the French Jesuit philosopher Pierre Teilhard de Chardin (1881-1955). All three engaged in fascinating discussions that led to a new description of the Earth's evolution. In addition to the existence of the geosphere, with its inanimate matter, and the biosphere, which describes the evolution of life, there was a development dominated by consciousness, mind, and interpersonal relationships, which the three thinkers called the *noosphere*. This vision represented a synthesis of the ideas of three figures from very different disciplines, although for Vernadsky the notion of the noosphere had a scientific meaning, while for Teilhard de Chardin it encompassed a more spiritual concept. It has sometimes been said that Vernadsky did with space what Darwin did with time: the latter showed that all life originated from a distant ancestor, whereas the Russian scientist believed that life originated from a single material, the biosphere[401].

After his stay in Paris, Vernadsky returned to Soviet Russia, settling in Leningrad in 1926 and in Moscow in 1935. His views as a moderate democrat were often criticized as too idealistic by the Marxist philosophers who had just entered the academy. He continued his studies, however, and the scientific prestige protected him from the party leadership. He wrote several books and contributed to nuclear research in Russia in the face of the growing threat of invasion by Nazi Germany. He was awarded the Stalin Prize in 1943. As the Cold War divided the geopolitical blocs, Vernadsky's work remained little known for a long time in the West, which was preoccupied with technological development and economic growth. However, his vision of the world was rediscovered in the 1970s and continues to inspire those interested in the place of living beings on our planet. It predated the term *Anthropocene*, introduced in 2000 by Paul Crutzen and the American limnologist Eugene Filmore Stoermer (1934-2012) to describe the geological period dominated by human activity.

Paleoclimatologists have long been interested in how the interactive processes specific to the *Earth system* have allowed life to persist on a planet throughout its geologic history. They also investigated the conditions favorable to the development of life on other planets, especially those outside our solar system. This last question remains unanswered to this day.

For several years, however, NASA was interested in the possible presence of living matter on other planets. That's why in 1965, as part of the preparations for the Viking mission to Mars, James Lovelock, whose work we mentioned in earlier chapters, was asked by NASA to answer a specific question: how can we

[401] Remarks attributed to the American biologist Lynn Margulis. Biogeochemistry - Biosphere - Noosphere: The Growth of the Theoretical System of Vladimir Ivanovich Vernadsky, George S. Levit in Studien zur Theorie der Biologie vol. 4.

detect the presence of living matter on a planet? The British scientist's answer was that the best signature of the existence of life is provided by the chemical composition of the planet's atmosphere. In fact, the existence of living matter is closely linked to the mechanism of photosynthesis, which transforms CO_2 from the air into organic matter and, at the same time, produces oxygen. This latter chemical constituent, if present in significant quantities in the atmosphere, testifies to the existence of life on the planet. Lovelock also noted that the evolution of the chemical composition of the Earth's atmosphere over more than three billion years allowed life to persist, even though when the first living things appeared, the Sun's luminosity was 30 percent lower than it is today. All other things being equal, the Earth's temperature at that time should have been about -33 °C, with ice-covered oceans and no liquid water. The explanation put forward by the American astronomer Carl Sagan (1934-1996) to resolve this paradox was that the amount of CO_2 in the primitive atmosphere was probably higher than today, and therefore the greenhouse effect was considerably more intense.

Lovelock and his collaborator, the microbiologist Lynn Margulis (1938-2011), introduced a concept that highlighted the properties of a system as complex as the Earth: the multitude of regulatory processes that keep climate variability within limits compatible with the continuation of life on Earth. These regulatory processes are associated with physical, chemical, and biological feedback mechanisms. When these feedbacks tend to stabilize the system and thus reduce the effect of the disturbances initially applied to the system, they are said to be negative. On the other hand, if they amplify these perturbations, they are said to be positive, and in this case, the system can eventually spiral out of control. There are a variety of feedback mechanisms in the Earth system, some negative, some positive, but currently the overall effect is a stabilizing one for the climate.

Numerous studies have attempted to identify the feedbacks that have influenced the climate evolution over successive geologic time periods. In the early 1980s, James Walker, Paul Hays, and James Kasting at the University of Michigan showed that the action of carbonic acid (H_2CO_3) (formed by the dissolution of atmospheric CO_2 in raindrops) on continental rocks (silicate $CaSiO_3$) produces calcium carbonate ($CaCO_3$), which is transported by rivers to the ocean. This calcium carbonate is then deposited on the ocean floor and gradually buried in the sediments, where it is transformed by metamorphism into calcium silicate rock ($CaSiO_3$), releasing CO_2 at the same time. This gas, initially buried in the Earth's crust, is eventually released into the atmosphere during periods of intense volcanic activity. The very slow transfer of CO_2 from the atmosphere to the depths of the ocean and then into the Earth's crust could have been responsible for a slow cooling of the planet, offsetting the gradual warming of the Earth resulting from the increase in solar luminosity. It is likely that, on a few occasions during the Proterozoic[402] era, atmospheric CO_2 levels were so low that the Earth became completely covered by ice. In the late

[402] Geological period extending from 2,500 to 540 million years ago. One of the most striking events seems to have occurred 600-700 million years ago. How life was able to perpetuate itself during these disrupted periods remains an area of research and debate.

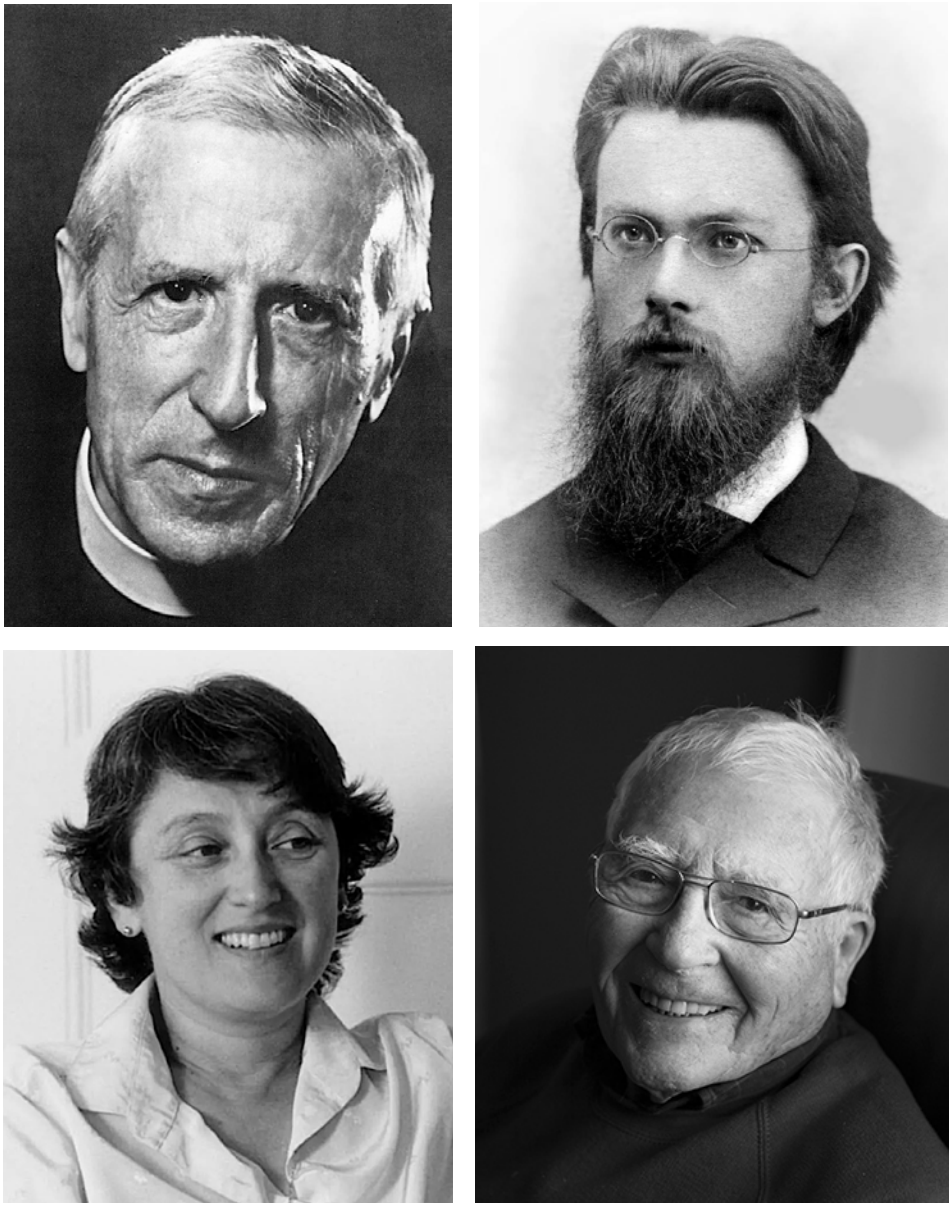
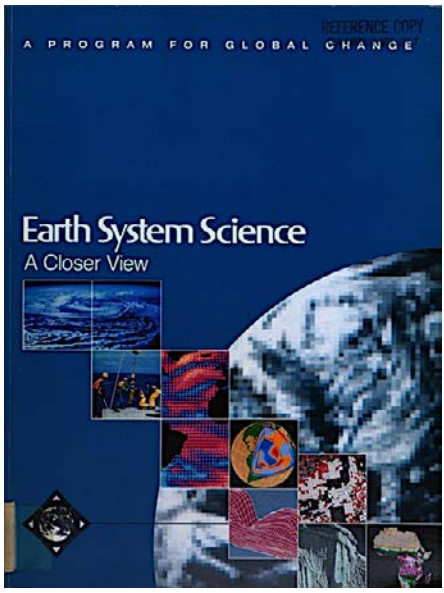


FIGURE 11.26: From left to right: Père Teilhard de Chardin, Vladimir Vernadskij (top), Lynn Margulis and James Lovelock (bottom).

1960s, Soviet climatologist Mikhail Budyko and his American colleague William Sellers independently demonstrated that this climatic condition, which turned the Earth into a giant snowball, was a stable planetary state. One had to wait for the return of intense volcanic activity with the release to the atmosphere of the large quantities of CO_2 buried in the depths of the Earth, to shift again to a warmer state of the planet, with a melting of the ice caps.

The regulatory mechanisms that characterize the Earth system can therefore occasionally be perturbed by the emergence of geophysical processes that disrupt the evolution of the planet, which researcher Tim Lenton describes as



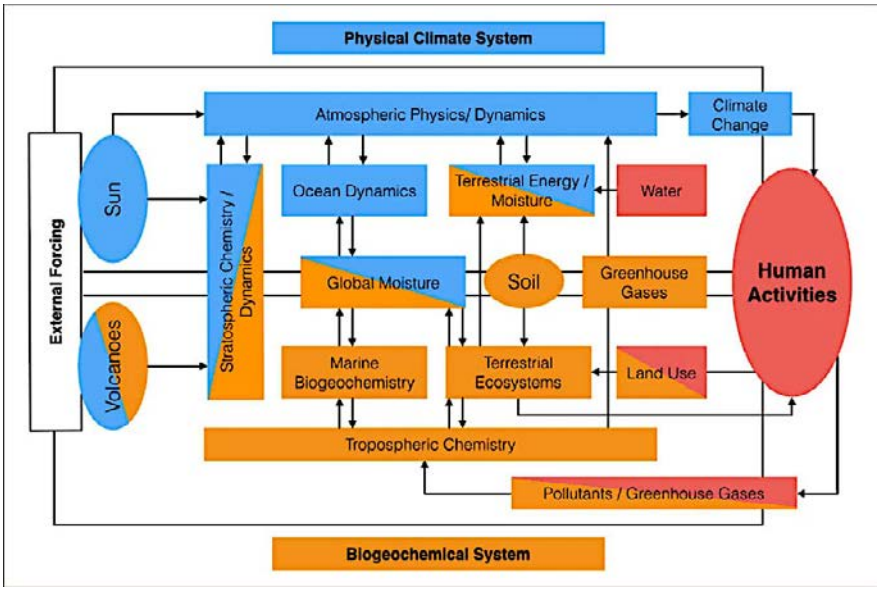


FIGURE 11.27: Left: Cover of a 1986 NASA report that offered a new perspective on "Earth System" research. Source: Overview of Earth System Science: A Program for Global Change (Washington, DC: NASA Advisory Council, 1986). Right: Simplified version of the Bretherton diagram adapted from the NASA report. Source: Steffen, W., Richardson, K. *et al*, The emergence and evolution of earth system science, *Nature Reviews Earth & Environment,* 1, 54-63, 2020.

planetary revolutionary events[403]. These include the appearance of life about 3.5 billion years ago, the initiation of photosynthesis probably between 3 and 2.7 billion years before our era, the great oxidation 2.4 billion years ago with the rapid increase in the amount of oxygen in the atmosphere and the formation of the ozone layer, and finally the appearance of the first creatures that consume oxygen to breathe. We should also mention the episodes of glaciation, and the agricultural and industrial revolutions that changed the face of the world. The fear today is that human activity will tip the Earth from the highly regulated system we know today to a new state far less hospitable to human civilization. The identification of possible tipping points affecting specific elements or regions of the Earth system (such as the Arctic or the Amazon rainforest) has become a major focus of research.

[403] Lenton, T., *Earth System Science. A Very Short Introduction*, Oxford University Press, 153 pp., 2016.

Epilogue
Advances in Knowledge

The journey we have just taken through the centuries has given us a better understanding, sometimes through stories, of how the atmospheric sciences have progressed since antiquity. By recounting the work of a few outstanding personalities, by describing the difficulties they encountered, and by evoking the exchange of ideas, the debates, and sometimes the controversies that have accompanied the progress of knowledge, we have tried to show how atmospheric science has progressed. The quest for knowledge has been a feature of all civilizations, but the conditions under which this knowledge has been acquired and transmitted have changed considerably over time. For this reason, the history of science is often presented in terms of three main periods[404]. The first, based on ancient Greek philosophy and continuing through the Middle Ages; the second, between the sixteenth and eighteenth centuries, based on measurement, experimentation, and early mathematical formalisms; and the third, from the nineteenth century onward, based on more quantitative methods. These were accompanied by greater specialization, leading to industrial and military advances and, more generally, to a new relationship between science and society.

Approaching a discipline through its historical development, rather than through the more systematic approach found in scientific treatises, makes it easier for non-specialists and students alike to tackle issues as complex as those covered in this book. Rather than presenting scientific concepts in the usual form of experimental data, daunting equations, or rigorous theories, we have opted for historical accounts that reveal the evolution of ideas over the centuries. By immersing ourselves in the historical context in which knowledge developed, we can appreciate the progressive nature of scientific advances and show the mutual influences between different disciplines. This approach to the development of knowledge highlights the evolution of the methodologies used by scientists in different eras: the hypothesis-deduction model typical of the Greco-Latin period, the recourse to the authority of a supreme being to explain the workings of the universe during the Middle Ages, and the systematic search for objective knowledge during the Renaissance. The European cultural movement of the nineteenth century saw the development of the scientific method,

[404] Gringras, Y., *Histoire des sciences*, Que sais-je?, Presses universitaires de France, 128 pp., 2026.

which used observation to formulate laws and theories and required verification of the quality of the data collected and the hypotheses adopted. According to Poincaré[405]:

> "Experience is the sole source of truth: it alone can teach us something new; it alone can give us certainty."

The historical approach taken in this book also allows us to place the progress of science within the socio-cultural, economic, and political framework of each era by examining the social norms to which researchers were bound. By recounting the work of the most eminent researchers, we have highlighted the successive stages that have shaped progress and, in particular, the paradigm shifts that have disturbed our civilization. These changes were sometimes accompanied by controversy among scientists and were not always readily accepted by society. Finally, scientific work has not been free of mistakes and wrong conclusions. In most cases, however, the lessons learned from these failures have enabled us to better understand future challenges and have demonstrated the importance of critical thinking and, in some cases, the need to question our certainties.

We conclude this book with a chapter that highlights the relationship between science and society, placing the progress of research in the context of the sometimes dramatic events that have shaken the world. Finally, we will point out that the study of the atmosphere is now part of a broader "Earth system" approach and that the scientific community, like society, is concerned about the global and regional changes resulting from human activities. The following text is therefore not a synthesis of the content of the previous chapters, but rather an introduction that attempts to place the issues surrounding "*The Air and Its Secrets*" in a broader perspective. It is intended to be a kind of essay, which to some extent reflects the personal views of the author.

Science Through the Ages

In Ancient Greece, after several thousand years of domination by the Babylonian civilization in Mesopotamia and the Egyptian civilization several thousand years before our era, science was primarily a philosophy and an art to which only a few independent scholars could devote themselves. In Athens, knowledge was transmitted from master to student in private schools. From the eighth to the twelfth century, during the Islamic period, knowledge was preserved in libraries. In the Middle Ages, the universities established in Europe became the places where culture flourished. During the Renaissance, religious courts dictated "truth". In the 18th century, however, the philosophical movement of the Enlightenment, which advocated reason, progress, and tolerance, led to the separation of church and state in Europe. This separation led to a desire for independence on the part of intellectuals. From then on, science was based on experimentation rather than the authority of ancient texts, which often contained religious teachings. From then on, knowledge was controlled by academies founded by princes and kings in many

[405] Henri Poincaré, *La science et l'hypothèse*, Paris, 1902.

parts of Europe. The autonomy gained by scientists, however, led to specialization in specific disciplines at the expense of the global vision of knowledge that had prevailed until then. In the twentieth century, it was once again the universities that catalyzed scientific progress, but governments and industry increasingly intervened in the organization of research, which had to support economic development, geopolitical superiority, military efforts, and, more generally, respond to the challenges posed by society. In addition to public research activities, the private sector set up its own laboratories to promote innovation and contribute to its development. In this context, universities and public research lost, to some extent their historical role of reference, as the intellectual curiosity and freedom of the researcher gave way to a contractual system, accompanied by periodic evaluations, in the hands of funding agencies. Since the end of the twentieth century, the trend toward more interdisciplinary research aimed at meeting the needs of society and supporting economic development, and the need to better communicate the knowledge acquired by researchers to the public, have profoundly changed the way universities operate and the way teaching is organized.

The progress made in understanding physical phenomena and chemical processes in the atmosphere is a perfect illustration of how science has evolved throughout history. Since the Renaissance, the scientific method has gradually replaced religious mysticism, but this transition has led to serious conflicts involving those who questioned the concept of divine revelation embodied in Church doctrine. The scientific work of previous centuries, carried out by a few motivated and enthusiastic intellectuals, who in many cases financed their own work and communicated with their colleagues through personal letters, gave way to research carried out in university laboratories and disseminated through specialized journals. This effort was greatly intensified after the Second World War, thanks to the explosion of technological resources.

The accumulation of knowledge over the centuries has not been a continuous, regular process. The "normal science" as called by the American philosopher Thomas Samuel Kuhn (1922-1996), i.e., research based on established values and a widely accepted reference model, has historically experienced crises that have periodically challenged its foundations[406]. The transitions, described by Kuhn as scientific revolutions, have profoundly changed not only the landscape of research but more generally, our view of the world. Examples include Copernicus' discovery of the Earth's orbit around the sun, Newton's laws of gravity, Lavoisier's substitution of phlogiston for oxygen, Maxwell's equations of electrodynamics, and Einstein's theory of relativity.

Antiquity

The inhabitants of our planet have always been interested in natural processes, especially astronomical and meteorological phenomena. Genesis in the Old Testament tells of the Flood, to which mankind tried to adapt, and the

[406] Kuhn, T.S., *The structure of scientific revolutions*, The University of Chicago Press, 1962.

concept is echoed in many ancient mythologies. Long before our time, great civilizations developed along rivers, notably the Nile in North Africa, the Tigris and Euphrates in Mesopotamia, the Ganges in India, and the Yangtze in East Asia. Data on geophysical disturbances and natural disasters were recorded by Babylonian magicians several centuries before the Christian era. Egyptian priests attempted to predict the date of the Nile flood, on which the lives of millions depended. Chinese imperial officials made meteorological observations more than a thousand years before our time.

However, it was in Ancient Greece, in the sixth century before our era, that science really took off. The idea that nature's behavior was determined by the will of the gods gave way to a more rational vision. Mysticism was replaced by a science that was initially highly empirical and included such illustrious names as Euclid, Archimedes, Thales of Miletus, and Pythagoras. For Aristotle, a follower of the rationalist approach, the natural motions of objects in the universe were the result of *laws* that operate without divine intervention. According to him, all motion required a cause, i.e., a motor, and when this cause ceased to act, motion continued only thanks to the action of air on the moving body. The vacuum, therefore, had to be considered non-existent, since, according to this formulation, the continued motion of an object in a vacuum was impossible. By introducing into his book on the universe the four natural elements (earth, air, water, and fire) that the Greek philosopher and poet Empedocles (~492-432 BCE) had invoked in the fifth century before our current era, Aristotle challenged for many centuries the "atomic theory" introduced by the philosopher Democritus (460-370 BCE). This theory claimed that matter consisted of small, indivisible particles surrounded by a vacuum. Aristotle was particularly interested in the interactions between air and water. However, the interpretation of natural phenomena was often arbitrary rather than based on systematic observations. Science at that time was essentially descriptive and empirical. Nevertheless, the four books that make up his work entitled "Μετεωρολογικά" (Meteorologica) remained an intellectual reference until the Middle Ages.

Founded by Alexander the Great in 331 BCE, the city of Alexandria became the great cultural and intellectual center of the Hellenistic Mediterranean, attracting numerous scholars who certainly benefited from the famous library established in the city in 288 BCE. The city was annexed by the Romans in 47 BCE. The Romans were primarily architects and builders, less interested in the sciences of the universe than in developing a vast infrastructure within their empire. Only a few writings, such as those of Seneca (3 CE - 64 CE) and Pliny the Elder (23-79 CE), refer to the natural sciences, but these are essentially limited to recalling the contribution of knowledge inherited from the philosophers of ancient Greece. In 59 CE, the philosopher and poet Lucretius, influenced by the principles of the Greek philosopher Epicurus (340-270 CE), one of the authors of the concept of atomism, wrote a work entitled *De rerum natura* (On the Nature of Things), in which he presented various terrestrial and celestial phenomena in the form of a long poem of 7,515 verses.

From the Eighth to the Fourteenth Century

The Golden Age of Science in the Islamic World and of the Scholastic Philosophy in the Christian World

With the decline of the Roman Empire and the conquest of Alexandria by the Arabs in 642 CE, Muslims gradually settled all the conquered lands, and intellectual activity shifted to the Arabian Peninsula. Between the eighth and fourteenth centuries, science advanced most rapidly in the East. The Arab-Muslim world was booming after the rise of Islam at the end of the sixth century, and scholars were interested in astronomy, mathematics, physics, geography, and medicine. Astrology and alchemy, inherited from Byzantium[407], were adopted by the Arab culture. Damascus became a center for a variety of cultures and traditions, while Baghdad, founded in 762 CE, welcomed scholars who contributed their knowledge. The House of Wisdom in Baghdad, built in the tradition of the Library of Alexandria, brought together scholars from all over the Muslim world to study the various sciences, especially astronomy. The Shamsiya Astronomical Observatory was built here in 828 CE. Arabic became the dominant language of science. Used in the production of numerous manuscripts, it enabled knowledge to be shared across a vast region stretching from the Iberian Peninsula to India and the borders of China. The Arab-Muslim civilization preserved and transmitted much of the scientific knowledge acquired in antiquity. In the ninth century, the Brethren of the Purity[408] in Basra, Iraq, published epistles discussing many disciplines, including meteorology. This secret society of Muslim philosophers was rationalist in outlook and largely based on Aristotelian ideas.

Meanwhile, Europe was going through a dark period, not very conducive to scientific research, dominated by religious beliefs and the primacy of the *First Being* of ancient Greece or the *God* of the Christians. Medieval alchemy, which developed under the impetus of the Persian scholar Jabir ibn Hayyan (c. 721-815 CE), aimed to produce the philosopher's stone[409] but also to create gold by transmuting metals and to prolong human life. Alchemy was practiced in India and China several centuries before the Christian era. Western alchemy, which originated in the fourth century in the Hellenic sphere of influence in Egypt before spreading to the Christian West with the Arab conquests of southern Europe, dominated European thought for much of the Middle Ages, combining spiritual and mystical considerations with material aspects.

From the twelfth century, the West acquired manuscripts from the Muslim world and translated them into Latin, thanks to the monks, thus benefiting from the knowledge acquired in the Arab world. Scholastic philosophy attempted to reconcile the principles of Greek philosophy with those of the Fathers of the

[407] Ancient Greek city at the entrance to the Bosphorus. Cosmopolitan city, capital of the Eastern Roman Empire, under Roman rule from the 1st century CE. Became Constantinople in 330 and Istanbul in 1930.

[408] Rasa'ula Ikhwan as-Safa is an encyclopedia of 52 treatises covering mathematics, natural sciences, psychology and theology.

[409] Hypothetical alchemical substance.

Catholic Church. Despite the creation of the first universities, the Catholic Church's relentless struggle against what it considered heretical currents prevented science from freeing itself from religious dogma. It also prevented scientific inquiry from being free and independent.

The Fifteenth Century

The Invention of Printing and the Discovery of New Continents

The fifteenth century, still marked by the Black Death that decimated Europe's population (1347-1352), was a century of transition between the Middle Ages and the Modern Age. Around 1460, Johannes Gutenberg (1400-1468), who lived in Mainz in the Holy Roman Empire, developed the printing press, a technology that would foster the development of science, and the Italian explorer Christopher Columbus (1452-1506) discovered America. For Europe, the 15th century was influenced by religious and occult beliefs, and the Renaissance, marked by the introduction of a cultural and scientific movement. This brought about a fundamental break in Western thought, placing humans at the center of reflection. This revival, which emphasized reason and people's ability to explain the world, inspired the revolutions to come. It led to major scientific advances, notably the mathematization of physics (which described the properties of bodies) and the replacement of alchemy by chemistry (which described the nature and transformation of bodies). The Renaissance was also a great moment for the arts, especially literature, music, painting, and architecture.

The Sixteenth Century

Heliocentrism Replaces Geocentrism

The 16th century saw the great explorations of the world, including the first circumnavigation of the globe by the Portuguese navigator Ferdinand de Magellan (1480-1521). It was marked by the Protestant reforms of Martin Luther (1483-1546) and John Calvin (1509-1564). It was also a time of great scientific exploration. For example, in Royal Prussia, part of the Kingdom of Poland, Nicolaus Copernicus (1473-1543) discovered heliocentrism[410]. This discovery was a true revolution, profoundly challenging the worldview and doctrines of the Roman Catholic Church. During this century, the Flemish mathematician Gerardus Mercator (1512-1594) introduced the geographical projection that bears his name and that would prove extremely useful to navigators crossing the seas. The 16th century was also marked by the work of the painter, architect, inventor, writer, and philosopher Leonardo da Vinci, who beautifully described natural

[410] The theory that the Earth revolves around the Sun was first evoked in ancient Greece by the astronomer *Aristarchus of Samos* (c. 310-230 B.C.). Copernicus, who became canon of Frombork Cathedral in 1501, published his theory in 1543 in his book "*De revolutionibus orbium cœlestium*".

processes in sketches and drawings that represented "visible truth" in addition to "scientific truth". For him, reasoning must be part of the experience that is the foundation of all inquiry. Da Vinci was particularly interested in the flow of water and air and insisted on the aesthetic character of turbulent motion. The mathematical sciences, he wrote, are not sufficiently concerned with the beauty of nature's works and the ornament of the world. In the middle of the century, Paracelsus (1494-1541) founded a new discipline: iatrochemistry, whose goal was to put chemistry at the service of medicine.

The importance of nature was emphasized in the literature of many countries. In early seventeenth-century England, the playwright William Shakespeare (1547-1616), influenced by the philosophers of ancient Greece, gave pride of place to the four elements invoked by Aristotle. In one of his last plays, The Tempest (1610), Ariel, the positive spirit of air and the breath of life, opposes Caliban, the negative character who symbolizes earth, violence, and death.

The Seventeenth Century

The Introduction of the Scientific Method

The seventeenth century marked the beginning of modern science. Francis Bacon (1561-1626) defined its principles. For this English thinker, often considered the father of empiricism, scientific knowledge must be derived from careful observation of nature, supplemented by inductive reasoning. In France, René Descartes (1596-1650), whose influence would be considerable for several centuries, claimed that humans can rely on reason alone (in opposition to Bacon's views on empiricism), and therefore do not need the enlightenment of faith. He distanced himself from Aristotelianism and scholasticism. Galileo (1564-1642) also challenged Aristotle's laws of motion. He showed that the motion of an object does not require a cause: it will continue uniformly if nothing accelerates or slows it down. The Italian scientist then introduced the law of falling bodies. Galileo's conclusions were taken up a few decades later by Isaac Newton (1643-1727), who established the foundations of classical mechanics and specifically the laws of gravity. He showed that the orbits of the planets were determined by the gravitational pull of the sun. In 1687, he published his famous work, *Philosophiae Naturalis Principia Mathematica*, or simply *Principia*, which revolutionized thinking. Newton's discovery of the universal laws of gravitation gave a scientific basis to physics, especially astronomy and meteorology. Newton was also interested in the nature of white light; after breaking it down with a prism to produce the colors of the rainbow, he introduced the Latin term *spectrum*, previously used to describe the appearance of a ghost. The discovery of the polychromatic nature of light paved the way for spectroscopy, a science that would not emerge until the early nineteenth century and would later be used to study the atmosphere of the Earth and other planets.

In Florence, Evangelista Torricelli (1608-1647) invented the barometer, which enabled Blaise Pascal (1623-1662) in France to demonstrate that air has a weight that decreases with height. The 16th century also saw the arrival of Johannes Kepler (1571-1650), who explained the orbits of the planets, and

Gottfried Wilhelm Leibniz (1646-1716), who took an interest in infinitesimal calculus and developed the mathematical tools needed to tackle the problems of mechanics. A new intellectual approach, fundamental to the development of knowledge and based on the mathematization of experimental information, made it possible not only to reproduce observations but also to predict the evolution of certain natural phenomena. Science progressed thanks to the creation of academies such as the Royal Society of London in 1660 and the Académie des Sciences de Paris in 1666.

It was also during this century that the first chemical constituents of air were identified, thanks to the studies of the Belgian Johan van Helmont, a follower of Paracelsus, who showed that combustion releases into the air what he called the *sylvester gas*. He was the first to demonstrate the existence of CO_2 in the atmosphere and is often considered the founder of *pneumatic chemistry*. The Irishman Robert Boyle, who rejected alchemy in favor of rigorous experimental methods, is one of the founders of modern chemistry. He also introduced the law that would become essential to meteorologists, showing the relationship between air volume and pressure.

The Eighteenth Century

The Age of Enlightenment and the Emergence of Scientific Disciplines

The influence of philosophers, writers, and composers, including Immanuel Kant (1724-1804) in Germany, Adam Smith (1723-1790) in England, and Voltaire[411] (1694-1778), Jean-Jacques Rousseau (1712-1778), and Denis Diderot (1713-1784) in France, Wolfgang Amadeus Mozart (1756-1791) in Vienna, and Johann-Sebastian Bach (1685-1750) in Leipzig profoundly marked the eighteenth century. Throughout this *Age of Enlightenment*, rationalism and individualism were pitted against the obscurantism of the Catholic Church and the arbitrariness of royal power. The freedom to question dogma and the respect for individual thought were to be protected. Knowledge replaced divine enlightenment, and the enlightened man was to oppose the masses who remained trapped in darkness. It was during this period of scientific flowering that the first great encyclopedias were published: First the *Lexicum Technicum*, published in 1704 by the English clergyman and scientist John Harris (1666-1719), then the *Cyclopaedia*, written in 1728 by the English publisher Ephraim Chambers (1680-1740), and finally *the Encyclopédie*, published in 1751 by Denis Diderot and Jean le Rond d'Alembert (1771-1783). This period also saw two revolutions that turned the world upside down and led to the advent of democracy: the American Revolution (1765-1791), which freed the states from British tutelage and paved the way for the creation of the United States of America, and the French Revolution (1789-1799), which abolished Royalty and established the Republic.

This was a propitious time for the development of science, and fluid mechanics in particular, thanks to the work of Joseph Louis Lagrange (1736-1813), who laid

[411] Voltaire's official name is François-Marie Arouet.

the foundations of analytical mechanics, and the Swiss mathematician Leonhard Euler (1707-1783), who used calculus to describe the flow of non-viscous fluids. Daniel Bernoulli (1700-1782) laid the foundations for the kinetic theory of gases. Meanwhile, observations by sailors provided the first description of atmospheric circulation on a global scale: warm air rises above the equator, giving way to cooler air from extratropical regions. According to George Hadley (1685-1768), it is the Earth's rotation that deflects these trade winds westward across the surface of the oceans. A new method of analyzing meteorological situations and their daily evolution was introduced: synoptic maps based on measurements transmitted by the nascent telegraph. A new idea was gaining ground: the importance of knowing the characteristics of past and present weather to be able to predict that of the future.

At a time when alchemy was being marginalized and the experimental method was being adopted by the scientific community, several new chemical substances were identified in the laboratory and great progress was made on the chemical nature of the gases that constitute the air. The two main gases in the atmosphere, nitrogen (Daniel Rutherford in 1772) and oxygen (Joseph Priestley in 1774), were identified. Henry Cavendish produced the combustible gas (hydrogen) in 1776, and Alessandro Volta isolated methane in 1776. It was against this background that pneumatic chemistry took off, and the concept of phlogiston, initially accepted by most scientists of the time, was challenged by Antoine Lavoisier (1743-1794), considered to be the father of modern chemistry. In 1733, Herman Boerhaave (1668-1738), a physician from Leiden in the Netherlands, introduced the concept of chemical affinity, and the French chemist Étienne François Geoffroy (1672-1731) used this notion to classify chemical substances according to their willingness to bond.

The Nineteenth Century

Triumphant Science and the Industrial Revolution

The nineteenth century was marked by the secularization of European societies. Philosophers and scientists took pride of place and enjoyed great independence and public esteem. Researchers, often from aristocratic and sometimes wealthy families, tended to work alone and received few resources from public authorities. However, they published widely in scientific journals, most of which were released by the Academies of Science. At that time, there was a quasi-religious belief in science and reason, which explains the flowering of the positivist movement introduced in France by the philosophers Saint-Simon[412] (1760-1825) and Auguste Comte[413] (1798-1857). This school of thought was an extension of the Enlightenment and was inspired by two main ideas. One was determinism, first proposed by Galileo, Newton, and Laplace, and the other was positivism, based on the progress of the human mind. This doctrine emphasized

[412] Claude-Henri de Rouvroy, Count of Sain Simon.
[413] Isidore Marie Auguste François Xavier Comte.

scientific laws to replace theological beliefs and metaphysical explanations. Émile Littré (1801-1881) defined positivism in a few sentences:

> "Positive philosophy is the totality of human knowledge, arranged in a certain order that enables us to grasp its connections and unity, and to draw general directions for each part as well as for the whole. It differs from theological philosophy and metaphysical philosophy in that it is of the same nature as the sciences from which it derives, whereas theology and metaphysics are of a different nature and can neither guide the sciences nor be guided by them; the sciences, theology and metaphysics have no common nature between them. This common nature exists only between positive philosophy and the sciences."

The century was also a period of great political instability, with the Napoleonic Wars and, after the fall of the emperor, the redefinition of the contours of Europe by the Treaty of Vienna, the rise of liberalism and the emergence of the social question[414], the first developments of socialism, the American Civil War and the abolition of slavery, and the formation of nation-states. The Industrial Revolution promoted the emergence of capitalism, which was well accepted in Anglo-Saxon countries thanks to the freedom of enterprise and the power of private property. By the end of the century, England, omnipotent thanks to its colonies, had to contend with competition from other nations, such as the United States, Germany, and Japan, which were fully participating in industrial development. These countries were experiencing rapid population growth and urbanization. At the same time, the desire to reduce the inequalities created by capitalism and the domination of the bourgeoisie fostered the emergence of the workers' movement. The new doctrines that took hold had a significant impact on the political models of nations.

Despite the armed conflicts that plagued Europe, the nineteenth century was a period of modernity, with major economic, commercial, artistic, scientific, and technological advances. The Industrial Revolution, symbolized by James Watt's (1736-1819) steam engine, not only created unprecedented economic dynamism but also disrupted landscapes and created air and water pollution that would affect future generations. The planet had just entered a new era that some now call the *Anthropocene*.

Ideas bubbled over, and scientific disciplines took shape. At first, thinking remained very Galileo-Newtonian, with a strong emphasis on classical mechanics, which perfectly reproduced the behavior of macroscopic objects. It was supplemented by a new concept, that of energy, which replaced the "caloric", hitherto considered as a fluid in motion, and by the arrival of a new discipline, thermodynamics, which combined energy and motion. It was also during this century that the theory of electromagnetism was developed at the instigation of the Scottish mathematician James Clerk Maxwell (1831-1879) and the Dutchman Hendrik Lorentz (1853-1928). In 1800, astronomer Friedrich Wilhelm Herschel discovered infrared radiation.

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[414] Refers to the social grievances by workers during the Industrial Revolution and led to population explosion.

In the face of the "mechanistic" vision inherited from previous centuries, a veritable revolution of ideas took place that would dominate scientific thought. This was the wave description of physical phenomena, which was applied to numerous disciplines such as optics, electromagnetism, acoustics, and hydrodynamics. This new concept took its roots in the work conducted during the 17th and 18th centuries. Christiaan Huygens (1629-1695), who saw light as an all-pervasive luminiferous ether, had developed a wave theory of light propagation, while Isaac Newton (1642-1727) had proposed a wave theory of sound propagation linked to the vibrations of particles in the fluid through which it travels. In the early 19th century, Thomas Young (1773-1829) in England and Augustin-Jean Fresnel (1788-1827) in France revived the theory of light waves. In 1887, the German Heinrich Hertz (1857-1894) demonstrated experimentally that light propagates as an electromagnetic wave, obeying the laws established by Maxwell and Lorentz. It appeared that light was part of a much larger electromagnetic spectrum. However, fifteen years later, still in Germany, Max Planck (1858-1947) argued that light is emitted in the form of energy quanta[415]. But it wasn't until the advent of quantum mechanics in the early twentieth century that the apparent wave-corpuscle duality was overcome.

In the mid-nineteenth century, Scottish physicist James Maxwell (1831-1879) and Austrian physicist Ludwig Boltzmann (1844-1906) introduced a statistical concept to describe physical phenomena by developing the kinetic theory of gases. English biologist Charles Darwin (1809-1882) formulated the theory of evolution. Around 1880, French chemist Louis Pasteur (1822-1912) developed the first vaccines against rabies. At the end of the century, physicists Marie Skłodowska-Curie (1867-1934) and Pierre Curie (1859-1906) began to study natural radioactivity. Wilhelm Conrad Roentgen discovered X-rays in 1895.

Thanks to advances in science, the nineteenth century was conducive to technological developments and the emergence of engineering. In 1837, Britain's first railroad was built between Manchester and Liverpool. Beginning in 1876, Thomas Alva Edison (1847-1931) developed electricity generation and distribution networks in the United States. He invented the incandescent light bulb, the phonograph, and the motion picture camera. Around 1875, Alexander Graham Bell (1847-1922) developed the telephone, which would change the way people communicated. Between 1859 and 1869, the diplomat Ferdinand de Lesseps (1805-1894) dug the Suez Canal, connecting the Mediterranean with the Red Sea. Between 1887 and 1889, engineer Gustave Eiffel (1832-1923) built an imposing metal tower that became the symbol of the city of Paris.

The atmospheric sciences benefited directly from these advances in science and technology. The concept of the electromagnetic spectrum paved the way for work on gas spectroscopy and, over the next century, led to the development of sophisticated techniques for measuring the chemical constituents of the atmosphere from the ground or space. The fundamental equations describing fluid flows were established and would, in the following decades, allow the development of rigorous methods for predicting the evolution of meteorological situations. The theory of thermodynamics was formalized thanks to the work of the French engineer

[415] A quantum is the smallest indivisible measure of a physical quantity such as energy.

Nicolas Léonard Sadi Carnot (1796-1832), the French physicist Émile Clapeyron (1799-1864), the German physicist Rudolf Clausius (1822-1888), and the Austrian physicist and philosopher Ludwig Boltzmann (1844-1906). The first principle of thermodynamics enabled meteorologists to express the transformation of solar energy into air movements and introduced the principle of equivalence between heat and mechanical energy. The second principle of thermodynamics established the notion of irreversibility of physical systems and introduced the concept of entropy. This principle states that any change in a physical system leads to an increase in disorder within that system. This discovery laid the foundation for chaos theory, which was established in the following century and changed the approaches to weather forecasts. The first studies of turbulence, begun at the end of the nineteenth century, continued into the twentieth century, thanks in particular to the work of the Soviet mathematics school.

Despite these theoretical advances in fluid mechanics and thermodynamics, the analysis of meteorological situations during the nineteenth century remained based on the subjective analysis of synoptic maps. Deemed less rigorous than astronomy or mathematics, meteorology was not immediately recognized as a science in its own right because it was unable to free itself from its empirical nature. Indeed, Robert FitzRoy based his first daily weather forecasts (1861) published in the London newspaper *The Times* on purely empirical analyses. It wasn't until the twentieth century that mathematical formulations expressing the fundamental laws of physics were applied to weather forecasting.

Significant advances were also made in the determination of the atmospheric chemical composition, with the discovery of the presence of ozone, carbon dioxide, various nitrogen and sulfur compounds, and certain hydrocarbons. The first studies of organic chemistry in the atmosphere were initiated. Measurements of the radiative properties of gases such as carbon dioxide and water vapor paved the way for scientific studies of the greenhouse effect, the existence of which had been suggested as early as 1824. It also led to a better understanding of the role of ozone in regulating solar radiation.

In short, the nineteenth century was an era of certainties brought about by a "classical science" that seemed to explain all of reality perfectly. For many, there was no longer the slightest gray area in our understanding of the phenomena taking place in the universe. This idea was, however, quickly abandoned at the beginning of the following century.

The Twentieth Century

Relativity, Quantum Mechanics, Nuclear Power, Space Exploration, Computers, and Climate Change

The twentieth century was marked by unprecedented ideological change and economic development, especially in the West. It saw the end of authoritarian and feudal regimes, but also the rise of totalitarianism, especially in Europe in the form of Fascism, Nazism, Populism, and Communism. The two world wars were responsible for massive destruction and the loss of tens of millions of

lives. Decolonization led to the emergence of newly independent countries. In many parts of the world, living standards rose, encouraging mass consumption, the development of a service economy, and the birth of a leisure civilization. Cultural production expanded with the rise of cinema, radio, television, computers, and the Internet. New forms of contemporary art and popular music emerged. Rapid economic and population growth reached their limits, leading to ecological awareness.

The Golden Age of Physics. The nineteenth century had been a triumphant era for science: the astonishing success of a mechanistic vision of the world left little room for the idea that another way of understanding reality was possible. For many, the end of that century left no gray areas in the understanding of physical phenomena. Yet, unexpectedly, the beginning of the twentieth century was marked by a revolution that profoundly changed our vision of the universe, replacing Newtonian mechanics and Maxwell's electromagnetism with a more abstract and symbolic way of describing reality. This revolution was associated with the names of Max Planck (1858-1947), Albert Einstein (1879-1955) and Werner Heisenberg (1901-1976) in Germany, Erwin Schrödinger (1887-1961) in Austria, Niels Bohr (1885-1962) in Denmark, and many other great figures of modern physics. Advances in science also came from Albert Einstein's theories of special relativity (1905) and general relativity (1915). Major advances in nuclear physics and radioactivity were due to the work of Pierre Curie and Marie Skłodowska-Curie[416], Henri Becquerel (1852-1908), Ernest Rutherford (1871-1937), Werner Heisenberg, and James Chadwick (1891-1974). In 1903, Pierre and Marie Curie were awarded the Nobel Prize in Physics, which they shared with Henri Becquerel for their work on radioactivity. Chadwick is credited with the discovery of the neutron in 1932, and the Hungarian physicist Leo Szilard (1898-1964) with introducing the concept of nuclear chain reactions in 1934. The fundamental work done in 1938 by Lise Meitner (1878-1968), Otto Hahn[417] (1879-1968) and

[416] Marie Skłodowska was born in Warsaw (Kingdom of Poland) in 1867. She completed her higher education in Paris (1891-1894). She collaborated with Pierre Curie, whom she married in 1895. She worked on natural radioactivity and discovered radium and plutonium. She was the first woman to hold a chair at the Sorbonne. She was also the first woman to win the Nobel Prize and, to date, the only woman to win two Nobel Prizes (physics in 1906 and chemistry in 1911). She died in 1934.

[417] Otto Hahn, winner of the Nobel Prize for Chemistry in 1944, was one of the directors of the Kaiser Wilhelm Society's Institute of Chemistry between 1928 and 1946. Initially located in Berlin, the institute was partially destroyed by an air raid in 1944. It was then moved to the former textile factory in Tailfingen, Württemberg. On April 25, 1945, at the end of the Second World War, Hahn was arrested in Tailfingen by the Anglo-American Alsos mission, set up to determine whether Germany was on the verge of developing atomic weapons. He was imprisoned with other scientists who had contributed to nuclear research under the Nazi regime. After brief stays in France and Belgium, the group of German scientists finally arrived at Farm Hall in Godmanchester, near Cambridge, UK, on July 3, 1945. Hahn was allowed to return to Germany on January 3, 1946. He was then invited to take over the presidency of the newly established Max Planck Society, successor to the Kaiser Wilhelm Society, which had been dissolved on February 26, 1948.

Fritz Strassmann (1902-1980) on the fission of heavy atoms (uranium and thorium), followed in 1939 by the studies of the French physical chemists Irène Joliot-Curie (1897-1956) and Frédéric Joliot-Curie (1900-1958), by the Italian-American physicist Enrico Fermi (1901-1954), and by Szilard on the production of secondary neutrons accompanying nuclear fission, led to the development of new sources of energy (nuclear reactors) from which society would benefit. But it also had a disastrous consequence: the development of the atomic bomb at the Los Alamos Center in New Mexico under the direction of the physicist J. Robert Oppenheimer (1904-1967). The world of quantum abstraction abruptly shifted to that of the use of nuclear energy for civilian and military purposes.

Advances in basic science led to extraordinary technological advances that benefited society. These included the development of electronic and optical compounds that paved the way for telephony, imaging, and television, the development of new materials, the revolution in transportation, with later the first voyages into space, and advances in medicine, with the production of new drugs and vaccines that have saved many lives. The identification of the structure of deoxyribonucleic acid (DNA) in 1953 by James Watson (b. 1928) and Francis Crick (1916-2004), winners of the Nobel Prize in Medicine (1962), and the discovery of penicillin in 1928 by the British physician and pharmacologist Alexander Fleming (1881-1955) were other major advances for human health. The last decades of the twentieth century saw impressive advances in fundamental biology, biotechnology, and medicine. Information theory and computer science were also developing rapidly.

Physics and chemistry were booming, and the most eminent scientists met several times in Brussels to discuss the latest advances at the conferences founded in 1912 by the Belgian industrialist Ernest Solvay (1838-1922). Basic research focused on the infinitely small phenomena of atomic, nuclear, and particle physics, molecular biology, and genetics, as well as the infinitely large phenomena of cosmology, astrophysics, and planetology. The Belgian physicist Abbé Georges Lemaître, who developed the Big Bang theory, and the American astronomer Edwin Powell Hubble (1889-1953) showed that the universe is expanding. The European Organization for Nuclear Research (CERN), founded in Geneva in 1954, still conducts fundamental research into the nature of our universe, specifically to identify the matter that it contains.

The scientific revolutions of the first half of the twentieth century led to a paradigm shift that fundamentally changed the way we think. The vision of a stable universe governed by immutable laws and completely predictable states gave way to one in which systems exist in a set of states that must be described probabilistically. The abandonment of the classical certainties to the forging of a more abstract reality of the universe left plenty of room for chaotic situations and called on mathematics to describe them. This is what the physicist

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In 1949, the Institute of Chemistry, now under the aegis of the Max Planck Society, moved from Tailfingen to Mainz. Among the atmospheric chemists who headed this institute were Christian Junge, Paul Crutzen and, more recently, Meinrat Andreae, Johannes (Jos) Lelieveld and Ulrich Pöschl.

Richard Feynman (1918-1988) wrote in his book *The Character of Physical Law*, published in 1965:

> "A philosopher once said: 'It is necessary for the very existence of science that the same conditions always produce the same results. Well, they don't!' "

Chaos theory, which challenged the deterministic certainties of Newton and Laplace, led to a breakthrough in fluid dynamics, and thus in meteorology, and in science in general. The contributions of Henri Poincaré (1854-1912) in France and Edward Lorenz (1917-2008) in the USA, fifty years later, were fundamental. For Ilya Prigogine (1917-2003), a specialist in dissipative structures and winner of the Nobel Prize in Chemistry, the theory of complex systems led us to rethink the notion of the *laws of nature*[418]:

> "The nineteenth century has left us a double legacy. On the one hand, we have the classical laws of nature, of which Newton's laws are the supreme example. These laws are deterministic: once the initial conditions have been given, we can predict any past or future event. They therefore speak of certainties. What's more, these laws are symmetrical with respect to time. Future and past play the same role.
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> But the nineteenth century also bequeathed us an evolutionary, temporal vision of the universe, through the second principle of thermodynamics. This principle expresses the increase in entropy over time and thus introduces an arrow of time. From then on, past and future no longer play a symmetrical role."

And Prigogine added a point that applies perfectly to the forecasts made daily by meteorologists:

> "In the history of physics, we have seen the successive appearance of the notions of trajectory, wave and field. [...] The introduction of instabilities such as chaos forces us to modify this vision. The fundamental level is now that of probabilities. [...] Little by little, a new rationality takes shape, in which probability is not ignorance, and science is not confused with certainty. It is at this price that the notion of evolution, and with it the notions of event and creativity, make their entry into the fundamental laws of nature."

Science in Support of Power. The twentieth century was also a period of great political upheaval and destructive armed conflicts. Twentieth-century research was profoundly affected by two world wars, which caused countless deaths and widespread destruction on most continents. Science and technology played a crucial role in these wars. World War I is sometimes called *the chemist's war* because chemists produced deadly gases that were dispersed over the battlefields. The 1939-1945 war, on the other hand, is often referred to as the *physicist's war* since several effective systems were engineered by physicists. This was the case of the radar-based aircraft detection systems initiated by the

[418] Prigogine, I., *Les lois du chaos*, Flammarion, Nouvelle Bibliothèque scientifique, Paris, 126 pp., 1993.

Scottish engineer Robert Watson-Watt (1892-1973) and of the nuclear weapons developed at the Los Alamos Center in New Mexico. The Manhattan Project began in 1943 with the goal of secretly producing an atomic bomb before the end of hostilities. It was also during this period that Germany, under the control of the Nazi government, developed and launched the first rockets. Military research paved the way for the exploration of space.

The era of scientism[419] and the researcher individualism that characterized the previous century was now over. Science had become dependent on political and geopolitical objectives, economic decisions, industrial priorities, and military strategies. It was directly affected by the budgets allocated in different countries. Government agencies now fund research efforts and, in effect, set priorities. Since research was no longer the sole province of specialists, the role of science changed considerably. The public's fascination with major technological achievements, such as space exploration and the development of medicine, coexisted with a more critical attitude toward researchers, sometimes questioning the results of their work; this skepticism, which persists today, often reflected concerns about poorly controlled or poorly accepted technological progress. Indeed, as the sociologist Edgar Morin[420] (b. 1921) suggested in 2022:

> "The tremendous development of the physical and biological sciences in the 20th and 21st centuries poses increasingly serious ethical and political problems. From the 17th century onwards, the sciences have been able to develop their autonomy only by eliminating all value judgments, i.e. all ethical and political judgments. Their role in the history of society gradually became immense. Progress in nuclear physics led to the creation, use and multiplication of nuclear weapons. Advances in quantum physics have led to the gigantic development of information technology. Advances in genetics, and more broadly in the biological sciences, have led to the manipulation of embryos and human beings.
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> Yet the sciences have no internal ethical safeguards. Ethics can only come from external morals, secular or religious. States are seizing the power of nuclear weapons, which have become a sword of Damocles for humanity. Profit is taking hold of genetics, turning researchers into businessmen, while medical research is being taken over by pharmaceutical multinationals dedicated to producing profitable cures at the expense of unprofitable ones. All these dangerous developments, aggravated today by the Covid pandemic, give a sombre topicality to Rabelais' old saying: 'Science without conscience is but the ruin of the soul' ".

Globalization of Science. In the first half of the twentieth century, the most important scientific discoveries were made by European researchers. The United States of America, realizing the importance of technological innovation,

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[419] A philosophical opinion which asserts that science provides us with knowledge of the totality of existing things, and that this knowledge is sufficient to satisfy all human aspirations.

[420] Morin, E., *Leçons d'un siècle de vie*, Pluriel, Paris, France, 147 pp., 2022.

gradually came to dominate the research effort in the second half of the century. The Cold War, which began in 1945, gave rise to a veritable arms race, with nuclear tests by the USSR, the United States, and China, as well as the exploration of space, whose objectives were often more geopolitical than scientific. The technological supremacy of the United States was the result of dynamic and ambitious scientific research, thanks to which the country exerted considerable economic and political influence throughout the world. On July 20, 1969, NASA astronauts Neil Armstrong (1930-2012) and Buzz Aldrin (b. 1930) became the first men to walk on the moon. American successes, supported by society, were made possible by the existence of a high-quality university system, national laboratories, generous funding for research, a willingness to collaborate between academia and industry, and a willingness to welcome intellectual elites from every continent.

By the end of the century, science had become global. Collaborations between researchers from different countries multiplied. Several Asian countries, including Japan and then China, increasingly contributed to the research effort. From 1977, under the leadership of Deng Xiaoping (1904-1997), China modernized. It invested heavily in basic and applied research, sent many of its students and researchers abroad for training, and encouraged its industry to invest in high-tech fields. Today, China has become the world's leading producer of scientific publications, overtaking the United States, which previously held the record. In Europe, scientific productivity remains high, but the effort required to translate knowledge into technological innovation remains insufficient, despite some undeniable successes.

Progress in Atmospheric and Climate Science. Atmospheric research has benefited directly from technological developments. After World War II, rockets - first German, then American, Soviet, French, British, Chinese, and Indian - made it possible to study air layers at high altitudes. Since the early 1960s, satellites have been used to observe the atmosphere from space. Laboratories and research centers have been established to study atmospheric processes, thanks to impressive technical resources and access to available platforms. Weather forecasting and the study of chemical composition also made extensive use of data collected by remote sensing from space. Laboratories often had access to extensive computing resources, particularly for storing and analyzing observational data.

Since the 1980s, the atmospheric sciences have undergone three successive revolutions. First, the implementation of increasingly sophisticated atmospheric *forecasting systems*, thanks to the development of increasingly powerful meteorological models that consider physical processes at increasingly smaller scales. The resulting success in weather forecasting can also be attributed to the progress made in integrating observational data into mathematical models. Then, since the 2010s, the *big data revolution* has allowed better use of large data sets, especially spatial data. Finally, since 2020, the use of *artificial intelligence* has increased significantly. This has made it possible to expand the scope of data interpretation and even to successfully predict the evolution of weather situations.

Climatologists benefited directly from these progress obtained by meteorologists. Beginning in the 1970s, atmospheric models were coupled with oceanic and continental models. These numerical tools consider increasingly sophisticated physical and biogeochemical processes and their interactions within the Earth system. These models, which require the use of supercomputers, make it possible to estimate climate development for the coming decades.

Towards Sustainability Science. The unbridled development of the capitalist, liberal economy, a source of both wealth and inequality, was fundamentally challenged by the famous *Club of Rome Report* published in 1972 by Donella Meadows (1941-2001), Dennis Meadows (b. 1942), and several of their colleagues. This document showed that the pace of economic growth, the unlimited use of the Earth's resources, and the speed of demographic development could not be sustained in a world of necessarily limited size and resources. As a result, the ecological movement took hold and influenced the direction of scientific research. This research focused not only on the physical, chemical, and biological processes of the Earth system, but also on the extent to which human activities affect the environment and society in general. The political world was challenged by these studies, and issues of sustainable development became increasingly important, particularly following the report entitled *Our Common Future*, published in 1987 by a UN commission chaired by former Norwegian Prime Minister Gro Harlem Brundtland[421].

A fundamental paradigm shift took place and challenged philosophical and religious doctrines, our cultures, our economies, and our ethics of life. The idea that human beings have a privileged place and the right to control nature, which had prevailed throughout history, was giving way to a more holistic vision that considered living beings as an integral part of the earth's environment. The anthropocentric vision, which certainly allowed remarkable scientific and technological progress in fields such as medicine, agriculture, industry, and transportation, but which also favored the unbridled exploitation of natural resources, was giving way to an era that advocated a balanced and sustainable coexistence between humans and nature. This profound philosophical shift emphasized our interdependence with the natural world. Every individual on the planet had to examine their ethical responsibilities and reflect on their new role in the sustainable development of our civilizations. For science historian Dominique Pestre[422],

> "Sustainable development is first and foremost, historically, a societal project, a choice for living together on Earth, an ideal given to guide collective action."

And for the environmentalist Edwin Zaccaï[423], sustainability is the new ideology of the twenty-first century, a principle of "good" that cannot be challenged

[421] Brundtland, G.H., *Our Common Future: Report of the World Commission on Environment and Development*, Geneva, UN-Document A/42/427, 1987. http://www.un-documents.net/ocf-ov.htm.

[422] Dominique, P., *À contre-science. Politiques et savoirs des sociétés contemporaines*, Éditions du Seuil, 251 pp., 2013.

[423] Edwin, Z., *Le développement durable, l'idéologie du XXIe siècle*, Sciences humaines, Grands dossiers, n° 14: Idéologies, le retour de flamme, 2009.

without risking rapid delegitimization. Jeffrey Sachs, an economist at Columbia University in New York, identifies six sectors of activity necessary for sustainable development: the knowledge economy, public health, industry and clean energy, sustainable agriculture, adaptation of urban infrastructures, and digital transformation.

Pestre associates three ideals with sustainable development: justice for the planet's population (present and future generations), the precautionary principle to be integrated into economic and social development, and the participation of all citizens in political decisions. However, this ideal is also a source of tension and conflict, since on the one hand, collective solutions come up against the logic of competition and rivalry for survival and dominance, and on the other hand, projects designed for the long term necessarily come up against the logic of immediate return on investment.

The concept of sustainable development, which emerged from the nuclear debates of the 1960s, the major environmental conferences of the 1970s (Stockholm, Rio de Janeiro), and the publication of several reports on the state of the planet, has also been targeted by organized opponents. The controversies surrounding climate change have been particularly heated, calling into question the methodology traditionally used by scientists concerned with environmental issues. The model by which researchers inform decision-makers of the results of their studies, in the hope that they will make desirable decisions, is now being challenged. Harvard professor and historian of science Naomi Oreskes sees several reasons for this phenomenon. One is that climate issues are complex and incomprehensible to the uninitiated. Second, the information provided by scientists directly or indirectly challenges powerful interests. In her view, opposition to the consensus of climate scientists by opponents who claim that the science is uncertain, and that climate change is of natural origin, is essentially politically motivated. This is particularly the case in the United States, where opposition in the 1980s was associated with the proponents of the Cold War, and in recent years with those of populism and nationalism. Although the concept of sustainable development has enabled many national and international institutions, including the United Nations, to develop a strategic vision, the concept remains fragile. It can be challenged by more immediate concerns or by political will. The drastic reduction of funding for US climate research in 2025 illustrates a worrying trend that seems to privilege the concept of post-truth over the scientific method.

Beginning in the 1960s, and in line with this evolution of ideas, the atmospheric sciences became more integrative and global. They sought to respond more effectively to the concerns of society. The new vision for the geosciences thus emphasized interdisciplinarity. By the end of the twentieth century, scientists had made significant progress in understanding the natural and anthropogenic mechanisms that are transforming the Earth system, particularly the planet's climate, and affecting both the biosphere and society. The goal is now to develop solutions to mitigate the effects of environmental change and to adapt to unavoidable climate change. The idea of implementing planetary engineering measures to counteract global warming is also being discussed. Climate control poses unprecedented ethical and political challenges.

The Twenty-First Century

Pressing Challenges for our Civilization

The beginning of the twenty-first century is marked by the convergence of social developments, technological advances, economic transformations, and environmental crises. Attitudes are changing, with a desire to recognize the diversity of individuals, promote their inclusion, and ensure gender equality. However, these concepts are being challenged by the resurgence of populism, fueled by the existence of migratory crises and demographic reconfiguration. The outbreak of the coronavirus in 2020-2021 has profoundly changed working conditions, encouraging the development of teleworking. This transition has been accompanied by an increase in automation and the omnipresence of digital culture. Instant communication between individuals has been enhanced by social networks, virtual reality, and the emergence of gigantic databases. The use of smart cell phones to transmit information instantly has profoundly changed human behavior. The Internet is ubiquitous, and artificial intelligence is performing tasks previously reserved for the human mind. These advances are taking place against a backdrop of redefined power relations between nations, the multi-polarization of the world, and the rise of China. Climate change and related extreme events are now a reality, requiring the implementation of systems that use solar and wind energy rather than fossil fuels, with the goal of reducing carbon footprints. Sustainable development is becoming a political goal.

The photograph of the Earth taken in 1972 by the astronauts of the Apollo 17 space mission made us aware of the complexity and fragility of our planet. It is unique in the solar system in its ability to support life. In his excellent essay *Earth System Science, a Very Short Introduction*[424] Tim Lenton (b. 1973) emphasizes the impact of earth photography on the inhabitants of the planet and the development of more integrated research.

> "When humanity first looked back at the Earth from space, the obvious unity of the planet that supports us—and all the life that we know of—entered the popular consciousness. Earth system science is the research field born out of this revelation —it seeks to understand how our planet functions as a whole system. The scope of Earth system science is broad. It spans 4.5 billion years of Earth history, how the system functions now, projections of its future state, and ultimate fate. It considers how a world in which humans could evolve was created, how as a species we are now reshaping that world, and what a sustainable future for humanity within the Earth system might look like. Earth system science is thus a deeply interdisciplinary field, which synthesizes elements of geology, biology, chemistry, physics, and mathematics. It is a young, integrative science that is part of a wider 21st-century intellectual trend towards trying to understand complex systems and predict their behavior."

[424] Lenton, T., *Earth System Science, A very Short Introduction*, Oxford University Press, 153 pp., 2016.

Is the state of equilibrium that characterizes the Earth system likely to change in the future as a result of external actions? Today, the main sources of global change are no longer natural forces such as variations in solar energy or volcanic eruptions, but perturbations associated with demographic change and human activities. We have entered the Anthropocene.

For Earth scientist Will Steffen[425] (1947-2023), the complexity of the *Earth System* must be considered if we are to find practical solutions to the problems of contemporary civilization:

> "Climate change has brought into sharp focus the capability of contemporary human civilization to influence the environment at the scale of the Earth as a single, evolving planetary system. Following the discovery of the ozone hole over Antarctica, with its undeniably anthropogenic cause, the realization that the emission of large quantities of a colorless, odorless gas such as carbon dioxide (CO_2) can affect the energy balance at the Earth's surface has reinforced the concern that human activity can adversely affect the broad range of ecosystem services that support human (and other) life and could eventually lead to a 'crisis in the biosphere'. But climate change is only the tip of the iceberg. In addition to the carbon cycle, humans are (*i*) significantly altering several other biogeochemical, or element cycles such as nitrogen, phosphorus and sulfur, that are fundamental to life on the Earth; (*ii*) strongly modifying the terrestrial water cycle by intercepting river flow from uplands to the sea and, through land-cover change, altering the water vapor flow from the land to the atmosphere; and (*iii*) likely driving the sixth major extinction event in Earth history. Taken together, these trends are strong evidence that humankind, our own species, has become so large and active that it now rivals some of the great forces of Nature in its impact on the functioning of the Earth system."

And he adds:

> "The concept of the Anthropocene, as it becomes more well known in the general public, could well drive a similar reaction to that which Darwin elicited. Can human activity really be significant enough to drive the Earth into a new geological epoch? There is one very significant difference, however, between the two ideas, Darwinian evolution and the Anthropocene. Darwin's insights into our origins provoked outrage, anger and disbelief but did not threaten the material existence of society of the time. The ultimate drivers of the Anthropocene, on the other hand, if they continue unabated through this century, may well threaten the viability of contemporary civilization and perhaps even the future existence of *Homo sapiens*."

Despite the importance of human activity in influencing planetary metabolism, the idea that humanity has entered a new geological epoch is not unanimous, especially among geologists. In 2024, after fifteen years of debate within

[425] Steffen, W., Grinevald, J., Crutzen, P., McNeill, J., The Anthropocene: conceptual and historical perspectives. *Philosophical Transactions of the Royal Society A 2011, 369*, 2011, https://doi.org/10.1098/rsta.2010.0327.

several groups, the Commission on Quaternary Stratigraphy of the International Union of Geological Sciences decided by 15 votes to 4, with 2 abstentions, to reject the concept of the Anthropocene. The main justification for this decision is that human activity began long before the dawn of the industrial age.

Scientific communication also evolved. The movement to open up science that began in the twentieth century continues. However, publications are now in the hands of powerful international publishing groups, often with open access. The results and data generated by public research belong to all citizens, who must have free access to them. Under the name of "citizen science", an international movement is emerging that invites citizens to participate directly in research, including the observation of phenomena affecting the planet. The participation of external groups in research, in private and public enterprises, enables the co-production of knowledge.

Future Challenges

Looking back at the progress of science since ancient Greece, we can see the colossal advances made in understanding the properties of air, its chemical composition, and its movements around the Earth. Many questions have been solved over the centuries thanks to the genius of a few scientists. At the beginning of the twenty-first century, several questions remain unanswered. What are the challenges for atmospheric and climate science in the coming decades?

First, fundamental research on atmospheric dynamics and physics will continue with the objective of understanding the mechanisms that generate fluctuations in air and water flows on different time and space scales. These include turbulence, convection, and cloud dynamics, as well as the role of gravity waves generated by the passage of air flows over terrain or by the presence of meteorological disturbances. Research will also focus on a better understanding of the interactions between the different atmospheric layers and between the atmosphere and the ocean. Progress is needed to improve the accuracy of weather forecasts, especially for severe phenomena such as hurricanes and tornadoes. Our understanding of cyclone and monsoon dynamics in the tropics and subtropics needs to be improved. The predictability of atmospheric conditions on time scales longer than a week remains an unresolved issue. The goal of some research centers is to predict the evolution of the Earth system on time scales ranging from seasons to decades.

With respect to the chemical composition of the atmosphere, and despite the progress made after the 1950s, many uncertainties remain regarding certain photochemical and microphysical processes. Specifically, we need to better understand the mechanisms that affect organic compounds in the atmosphere and the mechanisms that determine the chemical composition of aerosols and precipitation. Identifying and quantifying the sources, losses, and lifetimes of the species produced, whether of natural origin or associated with human activities, must be a priority. While the properties of chemical species in the gas phase are now relatively well understood, the physical and chemical processes associated with liquid and solid particles in the air, particularly the finest ones, will need to

be studied in greater depth over the coming decades. This includes studying the effects of aerosols and other pollutants on human health and the functioning of ecosystems, as well as understanding the relationships between the atmospheric chemical composition and climate at the regional and global scales.

The expansion of observing networks, including satellites, ground stations, and aircraft, is essential to improve data quality and coverage. Advanced data assimilation techniques will allow for better integration of observations into atmospheric models. Artificial intelligence will enable more efficient use of observational data and provide a new approach to improving weather and air quality forecasts.

Climate scientists will have to further investigate the mechanisms controlling biogeochemical cycles, especially the carbon and nitrogen cycles, the role of ocean circulation and the ice system in regulating climate, the processes related to the hydrological cycle (clouds, precipitation), the increase in extreme phenomena (storms, drought), and the impact of deforestation and urbanization. It is also important that they better understand the non-linearities inherent in the climate system. We need to determine whether small-scale factors are likely to lead to large-scale changes. Tipping points could affect the Amazon rainforest, the ocean circulation (particularly the existence of the Gulf Stream), the melting ice, and the disappearance of permafrost in polar regions.

Scientists must continue to inform the public about the dangers facing humanity if greenhouse gas emissions continue to rise. They will therefore have to provide governments, economic leaders, and all citizens with objective scientific information that will enable the implementation of ambitious policies to reduce greenhouse gas emissions. These policies must consider the existence of economic and social inequalities and promote genuine environmental justice at the level of nations and of their citizens.

The scientific community must also contribute to the implementation of adaptation measures. Climate change will have undesirable effects on people's daily lives. Some will probably have to leave geographical areas that have become uninhabitable and seek refuge in more hospitable regions. Economic sectors such as agriculture, transportation, and tourism will have to adapt to new situations.

Climate services, analogous to weather services, need to be established in all regions of the world to translate observational and modeled data into actionable climate information that enables informed decision-making to build resilience to climate change, facilitates community participation, and fills critical data gaps.

It must also be emphasized that communication between scientists and decision-makers cannot be a one-way street. It must take place in a spirit of cooperation and evolve into genuine collaboration. Today, climate science is no longer the preserve of geophysicists alone, but includes representatives of the economic, social, medical, political, and legal sciences. Climate research must therefore revolve around new concepts based on the "co-design" of programs and the "co-production" of knowledge with the participation of stakeholders. However, as Marcia McNutt[426], President of the American National Academy of Sciences,

[426] McNutt, M., Science is neither red nor blue, *Science, 386*(6723), 707, 2024.

stated, research must produce information, but it is up to policymakers to make the decisions that directly affect society:

> "Although science can affirm that climate change is happening and is primarily caused by anthropogenic greenhouse gas emissions, science can only predict the outcome of the various policies that might be enacted to address the problem. It is up to society and its elected leadership to decide how to balance these options, including the use of renewable energy, climate adaptation, carbon capture, or even various interventions that reflect sunlight back into space."

We can therefore conclude that knowledge has been greatly enriched over the past few centuries, thanks both to the ingenuity and insight of extraordinary individuals who have sparked scientific revolutions, and to the large number of researchers who have systematically observed our planet and the universe that surrounds it, then carefully analyzed and interpreted their measurements and the results of their models.

With all the knowledge we have gained over the centuries, we must wonder if knowledge will continue to advance. Should we expect new scientific revolutions, for example, the establishment of a unified theory of the universe? And if all fundamental questions have indeed been resolved, wouldn't we be witnessing the "end of science"? This is not the view of former *Nature* editor Sir John Maddox (1925-2009), who writes in his book "*What Remains to Be Discovered: Mapping the Secrets of the Universe, the Origins of Life, and the Future of the Human Race*":

> "500 years of modern science is a good start, but only a start."

While it is impossible to predict exactly how research will evolve, it is certain that science will continue to amaze us. Along with art and philosophy, it will allow the human spirit to flourish and society to evolve. By breaking down disciplinary barriers and proposing new approaches to solving fundamental problems and analyzing complex issues, science will continue to play an important role in our efforts to understand our global, regional, and local environments. The air will continue to hold secrets that science will strive to unlock.

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