

PATHWAYS OF DISCOVERY

The Ascent of Atmospheric Sciences

Paul J. Crutzen and Veerabhadran Ramanathan

Atmospheric science matters to everyone every day. It has been infiltrating public awareness lately for compelling reasons: the Antarctic ozone hole, global warming, and El Niño, a combined atmosphere-ocean phenomenon that causes severe weather. The first two are side effects of the industrial revolution, and El Niño is nature's warning against taking good weather for granted. Atmospheric science has become a multidisciplinary, high-tech activity rife with new and sophisticated instrumentation, computers, information technology, and measurement platforms, including satellites and aircraft.

Air chemistry (1–4), including the prediction and subsequent verification that chlorofluorocarbons (CFCs) destroy ozone, has recently moved to the field's forefront. Revelations about the susceptibility of people and ecosystems to both natural and humanly forced atmospheric changes also have been central. On a more purely scientific level, efforts to understand and predict the complex phenomenon of weather led to the discovery of chaos theory by meteorologist Edward Lorenz. Now, chaos theory helps physicists, chemists, biologists, economists, and many others striving to understand complex phenomena.

A comprehensive story about the ascent of atmospheric sciences over the past few centuries would fill library shelves. In these few pages, we first chronicle only a few developments in chemistry and meteorology up to the early 1970s, before the possibility of human influence beyond the local scale became actualized.

To illustrate how humanity's hand has grown to have global effects, we then zero in on two contemporary issues: atmospheric ozone and global warming.

Secret Air

Even by the mid-17th century, the properties of air had received remarkably little thought. Robert Boyle knew as much at the time as anybody when he opined that the atmosphere consists not of the "subtle matter," or ether, that his contemporaries presumed to fill the universe, but primarily of "exhalations of the terraqueous globe," that is, emanations from volcanoes, decaying vegetation, and animals. By the end of the 19th century, however, research into the nature of air already had proven invaluable.

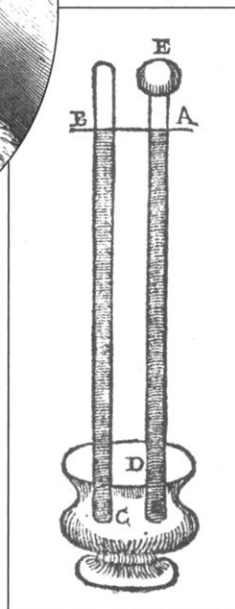
About a century ago, William Ramsay assessed the situation this way: "To tell the story of the development of men's ideas regarding the nature of atmospheric air is in great part to write a history of chemistry and physics."

Isolation of air's actual constituents began in the 18th century. Joseph Black identified carbon dioxide in the 1750s; Daniel Rutherford isolated nitrogen in 1772. A few years later, Carl Scheele and Joseph Priestley independently discovered oxygen. In 1781, Henry Cavendish established the composition of air to be 79.16% nitrogen and 20.84% oxygen regardless of location and meteorological conditions. By 1894 Lord Rayleigh and Ramsay had discovered argon in air. Thousands of chemical compounds have now been detected in the air, many at concentrations even less than 10^{-12} in molar mixing ratios (less than 1 part per trillion).

In 1839 (3), Christian Schönbein literally smelled a previously unidentified air component that would prove central to the scientific and public interest. During electrolysis experiments with water, he noticed a sharp odor. He ascribed it to a compound, which he called "ozone," after a Greek word meaning "ill smelling." In 1864 Jacques L. Soret recognized that ozone was the "dioxide of the O atom." In 1878, Alfred Cornu noticed the absence in sunlight of wavelengths shorter than 310 nanometers and postulated the presence of an absorbing gas in the atmosphere. Two years later, Walter N. Hartley measured the spectral properties of ozone and



Ocean of air. Using his newly invented barometer, Evangelista Torricelli began probing atmospheric pressure in the mid-17th century.



JANUARY
"Science Wars"

FEBRUARY
Planetary
Sciences

MARCH
Genomics

APRIL
Infectious
Diseases

MAY
Materials
Science

JUNE
Cloning and
Stem Cells

JULY
Communications
and Science

AUGUST
Quantum
Physics

SEPTEMBER
The Cell Cycle

OCTOBER
Atmospheric
Sciences

NOVEMBER
Neuroscience

DECEMBER
Astrophysics and
Cosmology

A Timeline of Atmospheric Sciences

c. 340 B.C.

Aristotle's *Meteorologica* is published; its theories remain unchallenged for nearly 2000 years.

1590s

Galileo Galilei invents the thermometer, a precursor of thermometers.

1643

Using a mercury barometer, Evangelista Torricelli performs experiments on atmospheric pressure.

1686

Edmond Halley shows that low latitudes receive more solar radiation than higher ones and proposes that this gradient provides forcing for the atmosphere's general circulation.

1714

Gabriel D. Fahrenheit develops the thermometer and a temperature scale.

1735

George Hadley introduces the importance of Earth's rotation in the features of major winds, including the easterly trades and the midlatitude westerlies; the tropical Hadley circulation is named after him.

1750s

Joseph Black identifies CO₂ in atmospheric air.

1770s

Daniel Rutherford identifies nitrogen in air. Carl Scheele and Joseph Priestley independently discover oxygen.

1781

Henry Cavendish measures the composition of air to be 79.16% nitrogen and 20.84% oxygen.

concluded that it was Cornu's absorber. The absorption of this ultraviolet (UV) radiation is essential for the survival of many of the planet's life-forms.

In 1902, Léon-Philippe Teisserenc de Bort discerned another important clue about ozone. Making measurements aboard a balloon, he found that at altitudes above 8 to 10 kilometers temperature did not further decline with altitude as it did at lower altitudes. He called this regime of more constant temperature, which is maintained by ozone's absorption of solar UV radiation, the stratosphere; the region below he dubbed the troposphere.

In the 1920s, Gordon M. B. Dobson measured the total amount of ozone in vertical columns of atmosphere. He found maximum amounts at higher latitudes and during early spring. These findings showed that stratospheric circulation plays a major role, implying upward transport from the troposphere to the stratosphere in the tropics with the return flow at middle and higher latitudes, the so-called Brewer-Dobson (after Alan Brewer) circulation. The theoretical framework for this circulation was developed over the next 50 years. A unified picture of the dynamical processes responsible for stratosphere-troposphere exchange of ozone and other gases was presented in 1995 by James Holton, Peter Haynes, Michael McIntyre, and their colleagues. The upward transport through the cold region of the tropical troposphere causes the stratosphere in general to be dry and cloud-free.

In 1930, the field of atmospheric photochemistry (3–5) began when Sydney Chapman proposed that ozone is produced photochemically from oxygen. Solar UV radiation with wavelengths shorter than 240 nanometers breaks O₂ molecules into two oxygen atoms, each of which then combines with another O₂ to yield ozone, O₃. The reverse process occurs when oxygen atoms from the photolysis of ozone react with O₃ molecules, resulting in O₂. David Bates and Marcel Nicolet extended this scheme in 1950 by showing that hydroxyl-based radicals derived from the photolysis of water molecules can catalytically convert ozone and atomic oxygen into O₂.

Air chemistry is just one—in fact one of the youngest—of the atmospheric sciences. The invention of the thermometer by Galileo Galilei and by others in the 1590s, and the 1643 invention of the barometer by Galileo's disciple Evangelista Torricelli, marked the start of experimental meteorology (6, 7). By the end of the 17th century, Edmond Halley had recognized the role of solar heating in the trade winds. His solar heat budget estimates revealed that the tropics receive much more solar radiation than the high latitudes. By the mid-18th century, George Hadley adopted Halley's idea and concluded that equatorial air must respond to the more intense solar heating first by rising and then by drifting poleward before returning to lower levels at the equator. Hadley also developed the correct explanation for the trade winds by deducing that Earth's rotation deflects the equator-directed surface flow toward the west relative to Earth.

During the 19th century, observational technology took another leap, this time in the form of instrumented balloons. Significant advances in observation tools took place during World War II, including weather radar and "radiosondes," or instrumented balloons bearing radio transmitters. The new observations revealed large, longitudinally asymmetric mo-

tions in the atmosphere, such as extratropical cyclones, and the midlatitude jet stream. Armed with the new data, Jacob Bjerknes, Carl-Gustaf Rossby, and Jule Charney transformed the science of atmospheric motion into its modern form between 1920 and 1970 (8, 9).

Basically, the equator-to-pole gradient of radiative heating that Halley discerned leads to gradients in temperature, potential energy, and zonal air flows, such as the upper troposphere jet stream. The jet is unstable to small perturbations, and the resulting wavelike eddy motions grow and concentrate temperature gradients to form narrow warm and cold fronts, which generate much of local weather. The poleward transfer of heat in the extratropics is accomplished by these eddies, without which the polar regions would be more than 50°C colder and the tropics would be much hotter.



Savvy Svante. A century ago, Svante Arrhenius saw how the atmosphere and surface temperature were linked.

With a theoretical foundation for atmospheric circulation coming into place, another question arose: How is surface temperature regulated (10)? Jean-Baptiste Fourier suggested in 1824 that the atmosphere behaves like the glass cover of a box exposed to the sun by allowing sunlight to penetrate to Earth's surface and then retaining much of the "obscure radiation" (wavelengths greater than about 4 μm that emanate from Earth's surface). By the mid-19th century, John Tyndall had demonstrated that the key process retaining this long-wave radiation is its selective infrared (IR) absorption by atmospheric H₂O and CO₂.

Constructing such greenhouse models of the atmosphere required accurate measurements of solar and IR transmission. That's where Samuel Langley's observations of lunar and solar spectra from 1885 to 1890 came in. Those data, and the identification of numerous H₂O and CO₂ absorption bands in spectroscopic measurements, set the stage for the famous study in 1896 by the Swedish chemist Svante Arrhenius. He developed a detailed model for the surface-atmosphere radiation budget and used it to reveal the large sensitivity of surface temperature to increases in atmospheric CO₂. Arrhenius included the positive feedback due to water vapor (the dominant greenhouse gas), whose atmospheric loading increases with temperature because of the increase in saturation vapor pressure with temperature. As a result, a water-vapor-based greenhouse effect increases with a warming.

In 1967, Syukuro Manabe and Richard Wetherald reformulated the greenhouse theory. They demonstrated that surface temperature is not determined solely by the energy balance at the surface (as assumed by Arrhenius and others), but also by the energy balance of the surface-troposphere-stratosphere system. The underlying concept is that the surface and the troposphere are so strongly coupled by convective heat and moisture transport that the relevant forcing governing surface warming is the net radiative perturbation at the top of the troposphere. This concept of a radiative-convective equilibrium, which is used extensively in astrophysics, was originally proposed in 1862 by Lord Kelvin to explain the temperature decrease in the troposphere.

Another big part of the atmospheric and climate equations is clouds (10). For decades, models have predicted that clouds have a net cooling effect. Data from the NASA Earth

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Radiation Budget Satellite Experiment confirmed those predictions in 1989. The data reveal that solar radiation reflected by clouds exceeds their greenhouse effect by a significant 15 to 20 $\text{W}\cdot\text{m}^{-2}$ —a cooling effect about five times larger than the warming effect from a doubling of CO_2 . Small changes in cloudiness, therefore, can have large but uncertain feedback effects on climate. A comprehensive study by Robert Cess and colleagues in 1990 revealed that cloud feedback simulations using so-called general circulation models (GCMs) yield varying results. Until there is a theory or a model of the hydrological cycle that can accommodate the scales of all cloud systems—from tens of meters (cumulus) to more than 1000 kilometers (tropical cirrus)—rigorous climate prediction will remain out of reach.

There are other obstacles that have been keeping a detailed quantitative understanding of climate and the general circulation at bay. After all, these phenomena depend on numerous complex physical processes, among them radiative transfer; land surface processes; and the formation of clouds, ice, and snow cover. Computers began coming to the rescue in the mid-1950s, and thanks to their ever-increasing power, today's GCMs are starting to account for many of these processes, albeit not reliably yet. In the 1950s, weather prediction drove the development of GCMs (by Jule Charney, John von Neumann, and Norman Phillips), but once such models were available they were put to wider use for such tasks as simulating general atmospheric circulation, climate, and global warming.



Acid rain fallout. Red spruce trees suffer from pollution in the Great Smokey Mountain National Park.

Growing Impacts of Human Activities: Ozone and CFCs (4, 5)

Air pollution is as ancient as the harnessing of fire for cooking, heating, smelting metal, and clearing land. Diminishing wood resources in some European locations within the past millennium spurred coal use and with it a rise in sulfur-based air pollution, which has led to one of the most publicly recognized forms of pollution—acid rain.

Coal use increased 500-fold during the industrial period. The dearth of control and regulation enabled urban air pollution to worsen into a major problem, culminating in the killer smog of 5 to 9 December 1952 in London: An estimated 4000 people died because of it. Since then, legislation has been passed to prevent a repeat. Still, with the continuing growth of coal and oil use in North America and Europe, and the construction of high chimneys to alleviate local pollution, the problem of acid rain has grown to international dimensions.

Based on data from a network of sites in Europe, which was established in the 1950s by the International Meteorological Institute in Stockholm, Svante Odén showed that

highly acidic precipitation had spread to much of northern and Western Europe by 1968. Ecological consequences, such as forest decline and fish deaths, were most pronounced in the Scandinavian countries. The problem gained international attention in 1972 with the presentation of a Swedish study at the first U.N. Conference on the Human Environment in Stockholm. This study made a strong case for reducing sulfur emissions. Since then, Europe and North America have made considerable progress, but the use of sulfur-rich coals in parts of Asia is leading to a repeat of regrettable history.

In the 1940s and 1950s, the Los Angeles Basin began suffering from a new kind of air pollution, especially during sunny summer days. It caused poor visibility, eye irritation, and crop damage. Arie Haagen-Smit showed that this type of pollution could be simulated by irradiating mixtures of air and car exhaust with sunlight. "Photochemical smog" has now become commonplace around the world.

By 1970, the chemistry of ozone production near the surface (often called "bad" ozone, compared to the "good" ozone in the stratosphere that absorbs harmful solar UV radiation) had been identified. It begins with the attack by hydroxyl radicals (HO) on hydrocarbons or carbon monoxide, producing peroxy-radicals. These radicals donate O atoms to O_2 to form ozone, whereas NO and NO_2 are catalysts for ozone formation. The hydroxyl radicals themselves are produced when solar UV radiation infiltrates mixtures of ozone and water vapor in air.

Hiram Levy pointed out in 1972 that these radicals play a major role in atmospheric chemistry. Despite their rarity (the average molar mixing ratio of HO in air is 4×10^{-14}), they are known as the "detergent of the atmosphere." The lifetimes of most gases—whether derived from natural processes or human activities—are determined by their reactivity with HO and can vary from hours to years. Some gases, such as CFCs and nitrous oxide, do not react with HO. That's how they end up being so influential in stratospheric ozone chemistry.

Tropospheric ozone (about 10% of total atmospheric ozone) is central to atmospheric cleaning because of its role in creating HO. Contrary to the widespread belief that tropospheric ozone originates in the stratosphere, one of us, Paul J. Crutzen, proposed in 1972 that the global troposphere itself is an important source of its own ozone and that human activity plays a major role.

The argument was based on tropospheric NO_x ($\text{NO} + \text{NO}_2$), much of which is produced by the burning of fossil fuel and tropical biomass. Depending on NO_x concentrations, large amounts of ozone can be produced or destroyed during the oxidation of ever-present carbon monoxide (CO) and methane (CH_4), levels of which have been rising. Together, these conditions have led to a substantial increase in tropospheric ozone, especially in the Northern Hemisphere. The tropics and the Southern Hemisphere also are influenced by human activity through extensive burning of biomass.

Human activity influences stratospheric ozone as well. In 1970, Crutzen and Harold Johnston called attention to the catalytic role of NO_x in controlling levels of stratospheric ozone and to the possibility of ozone destruction by NO-emitting supersonic aircraft. The rate-limiting reaction is $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$. The oxygen atoms come from the photolysis of O_3 , and the NO_2 comes from the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$. The net result is $2 \text{O}_3 \rightarrow 3 \text{O}_2$ or, in other words, ozone destruction.

Clearly, the role of NO_x species as catalysts in ozone chemistry is complex. We now know that above about

1839

Christian Schönbein discovers ozone in the laboratory.

1859

John Tyndall suggests that water vapor, CO_2 , and any other radiatively active ingredient of the atmosphere could produce "all of the mutations of climate which the researches of geologists reveal."

1878

Alfred Cornu measures the spectrum of solar radiation reaching Earth's surface and suggests that the absence of short-wave ultraviolet radiation is due to an atmospheric absorber. Two years later, Walter Hartley concludes that Cornu's absorber is ozone in the upper atmosphere.

1896

Svante Arrhenius publishes a climate model demonstrating the sensitivity of surface temperature to atmospheric CO_2 levels.

1919–25

Jacob Bjerknes, his father Vilhelm, and Halvor Solberg develop polar front theory for describing local meteorology.

1919–37

Vilhelm and Jacob Bjerknes and others identify extratropical cyclones as waves on the polar front. Together with later planetary wave theories by Carl-Gustaf Rossby and Jule Charney, these atmospheric motions provide the modern-day dynamical foundation for understanding general circulation and weather forecasting.

1920

Milutin Milankovitch publishes his theory of ice ages based on variations in Earth's orbit.

1924–28

Gordon Dobson documents the latitudinal and seasonal variation of ozone.

1928

Gilbert Walker describes the "Southern Oscillation," the saw pattern of atmospheric pressure on the eastern and western sides of the Pacific Ocean.

1930

Sydney Chapman proposes the first photochemical theory for upper atmospheric ozone production.

1941

Radar is used for weather tracking.

1949–56

Work by Alan Brewer and Dobson leads to a model for stratospheric general circulation.

1950

David Bates and Marcel Nicolet propose that H , HO , and HO_2 play a catalytic role in the atmosphere.

Charney and John von Neumann demonstrate the science of numerical weather forecasting with the ENIAC computer.

1956

Norman Phillips completes the first successful numerical simulation of atmospheric circulation.

1959

The Explorer VI satellite provides TV imagery of cloud cover. Verner Suomi uses Explorer VII to estimate the global radiation heat budget of the Earth-atmosphere system.

25 kilometers, NO_x catalyzes ozone destruction, but that the opposite holds at lower altitudes. The biosphere also is involved in the natural control of stratospheric ozone. That's because stratospheric NO forms by the oxidation of N_2O , which is produced largely by microbes in soils and waters. This is just one of many ways in which the biosphere is involved in atmospheric chemistry and climate, a complex dynamic most fully developed by James Lovelock in his much-debated Gaia hypothesis, which invokes self-regulating relations between atmospheric chemical composition, the biosphere, and climate.

As it turned out, large supersonic fleets were never built, but the research that emerged because of that possibility greatly improved knowledge about the stratosphere's chemistry and dynamics. This was important because in the meantime an enormous time bomb already had been ticking for several decades.

After their introduction in the 1930s as better and safer refrigerants, emissions of the CFCs CFCl_3 and CF_2Cl_2 began increasing. In 1972, Lovelock made the first worldwide CFC measurements on a research ship between England and Antarctica using his powerful electron capture technique, allowing measurements of gases with molar mixing ratios in the 10^{-12} range and below. He concluded from his data that CFCl_3 was accumulating in the atmosphere, but without consequences for the environment. Two years later, however, Mario Molina and F. Sherwood Rowland pointed out that when CFC gases break down in the stratosphere, they produce Cl and ClO . These radicals then attack ozone catalytically much as do NO and NO_2 , but even more effectively.

With unabated CFC emissions, calculations suggested that ozone depletion would peak at altitudes near 40 kilometers, causing local losses up to some 30% to 40% after several decades. By the late 1970s, several nations, including the United States, Canada, Norway, and Sweden, had responded to this alarming finding by forbidding the use of CFC gases as propellants in spray cans. Their use for other purposes continued, however.

One reason for this modest response was that the Molina-Rowland mechanism was thought to result in ozone depletion largely above 30 kilometers. Most ozone is located at lower altitudes, however. And there, formation of the rather unreactive molecules, ClONO_2 and HCl , protects ozone from otherwise much greater destruction.

This sense of complacency rapidly evaporated in 1985 when Joe Farman of the British Antarctic Survey and colleagues published a most surprising set of measurements (see figure). Their data revealed 40% depletion of total ozone during austral spring compared to levels measured since 1956 at the Halley Bay Station in Antarctica. These depletions were much greater than predicted, and they occurred in a geographic region where such depletions were unexpected.

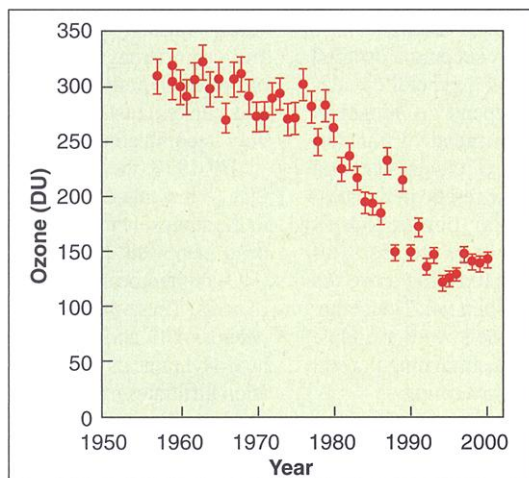
Subsequent measurement campaigns in the Antarctic—headed by David Hofmann, Susan Solomon, and James Anderson—revealed that the greatest ozone depletions occur at altitudes between 12 and 22 kilometers, exactly the range of naturally maximum ozone concentrations. Also, ClO and OCIO radicals were found to be far more prevalent than predicted, suggesting that new chemistry was afoot. Solomon, Rowland, and their colleagues proposed that under the cold conditions prevailing in the ozone hole region, HCl and ClONO_2 molecules react on ice particles to yield Cl_2 , which in sunlight dissociates rapidly into two ozone-destroying Cl atoms.

Through laboratory simulations Luisa and Mario Molina discovered yet new ozone-depleting catalysis, this one involving the reaction of ClO with another ClO as the rate-limiting step. This chemistry is especially important at altitudes below about 25 kilometers. Because annual increases in stratospheric chlorine were exceeding 5%, ozone depletion was increasing by twice that much. The Molinas' study and many others show the great importance of laboratory simulations of chemical reactions of atmospheric interest (11, 12).

Further research showed that the chlorine activation reactions could occur on solid or supercooled liquid particles containing mixtures of water and sulfuric and nitric acids. Such particles can form at temperatures about 10°C higher than the freezing point of water ice from sulfuric acid-containing aerosol. They also can be players in the Arctic. Depending on temperatures, ozone losses of up to 30% have occurred there in some years during the past decade in late winter to early spring. Total ozone loss over the Antarctic has been reaching the yet more dramatic levels of 50% to 70% each year during spring. After the discovery of the ozone hole, international regulations to limit CFC production picked up speed, resulting in a total phase out of production in the industrial world since 1996.

It is hard to tell if stratospheric ozone destruction or global warming is more sinister in the public mind. The realization that a doubling of CO_2 would warm the globe significantly inspired Arrhenius to resurrect Tyndall's suggestion that history's glacial epochs may be due to large reductions in atmospheric CO_2 . Another impetus for investigating the connection between CO_2 and surface warming was Guy S. Callendar's conclusion in the late 1930s that fossil fuel combustion had been increasing atmospheric CO_2 . In 1958, Charles D. Keeling began continuous measurements of CO_2 at the Mauna Loa Observatory and demonstrated beyond any doubt that CO_2 is increasing at a rate of about 1.5 parts per million (ppm) per year due to anthropogenic activities (see figure on p. 303).

Then came Manabe's and Wetherald's 1975 GCM study, which showed that doubling CO_2 can warm the globe by up to 3 K. Nearly simultaneously, the global warming problem took off in another attention-getting direction. One reason was the identification by one of us, Veerabhadran Ramanathan, that CFCs have a direct greenhouse effect and that a molecule of CFCl_3 or CF_2Cl_2 was about 10,000 times or more effective than a molecule of CO_2 at enhancing the greenhouse effect.



Oh-oh-zone. Total column ozone measured in October at Halley Bay, Antarctica, from 1956 to 1994. One DU, or Dobson unit, is the equivalent height the total ozone in the column would have (in 0.00001 m) if it were compressed to 1 atm at 273 K.

In 1976, CH₄ and N₂O joined the list of greenhouse gases. A few years later, tropospheric ozone also joined the list, which has grown to include several tens of greenhouse gases. These developments culminated in an international study in 1986 (13) sponsored by the World Meteorological Organization. The study concluded that the non-CO₂ gases significantly added to the warming by CO₂. The global warming problem suddenly had become more urgent.

The urgency was further accentuated by the fact that the surface warming trend, which began in the 1970s and continued unabated into the 1990s, had reached the point where the global mean surface temperature was higher than ever recorded during the 20th century. James Hansen undertook GCM simulations that included observed trends in CO₂ and other trace gases. The simulated temperature trends supported scenarios in which the human input of such gases indeed was the cause of surface warming, a finding that placed global warming higher on the political agenda. The problem's global nature demanded international reviews. So in the late 1980s, the Intergovernmental Panel on Climate Change (IPCC) was established to make a comprehensive assessment (14). It concluded that "the balance of evidence suggests a discernible human influence on global climate."

That point coincides with the finding that global warming is also influenced by stratospheric ozone depletion. As shown by Venkatachalam Ramaswamy, for example, the observed lower stratospheric cooling during the 1980s and 1990s is explained by the radiative response to ozone destruction, a process carrying implications for tropospheric climate as well.

An Uncertain Future and the Need for Synthesis

We start the new century with formidable environmental challenges that affect the welfare of all humans. On the potentially positive side, stratospheric ozone could recover and the ozone hole could disappear by midcentury, although we cannot rule out the possibility of it becoming worse before it gets better due to cooling of the stratosphere by increasing CO₂. On the negative side, by the early 22nd century, atmospheric CO₂ is expected to double from its concentration of 280 ppm (14) prior to inputs from human industry.

Unfortunately, the negative possibility seems a good bet. After all, nearly 75% of the world's population by then, which is projected to approach 10 billion people, will be striving to match Western standards of living. Those efforts will likely entail enormous additions of atmospheric pollutants, land surface alteration, and other environmental stresses. The net radiant heat added to the planet (since 1850) by greenhouse gases is likely to

amount to at least 4 W·m⁻². According to our best understanding of the system, that could warm the planet by about 1.5 to 3 K, depending on competing effects from aerosols. The atmosphere and the planet, it would seem, are headed toward uncharted territory.

One of the major surprises could very well be the response of El Niño (15) to such a warming. Warren Washington and Gerald Meehl have proposed that global warming can lead to an increase in the frequency of El Niños through feedback mechanisms involving clouds and ocean circulation in the Pacific. It may well be argued

that the environmental expansion of human activity has jolted Earth into a new geological era, the "Anthropocene."

Temptations to engineer the atmosphere to mitigate the negative effects of human activities could become enormous. Might it be possible to combat global warming by burying CO₂ in the deep ocean, or by supplying iron to parts of the ocean to increase photosynthetic and oceanic CO₂ uptake, or by adding light-scattering particles to the atmosphere to scatter sunlight back into space? How about adding propane to counter stratospheric ozone loss? The practicality, cost, and side effects of such efforts pose major problems. We focus here instead on the scientific issues

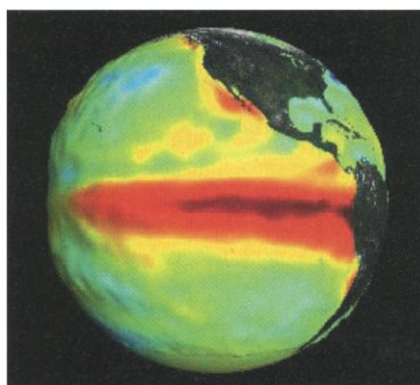
that may help us anticipate our future challenges.

The air, whose composition is a product of biological and industrial processes and of atmospheric chemistry, is a primary factor for Earth's climate and our health and quality of life. This system can only be effectively studied within the broader context of the biogeochemical cycles of carbon, sulfur, and nitrogen, all of which have been perturbed by human activity.

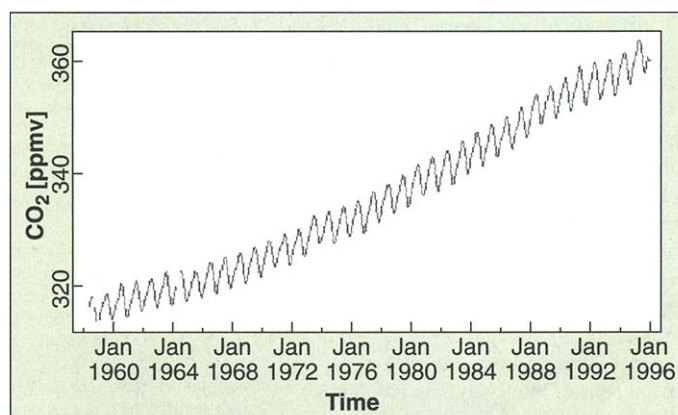
We've already noted how variations of atmospheric CO₂ are linked with such life-defining phenomena as glacial-interglacial cycles (see figure on p. 304) and surface temperature. Although the variation in solar insolation caused by orbital changes is the basic forcing mechanism for the glacial-interglacial cycles (as originally suggested by James Croll in 1864 and showed quantitatively by Milutin Milankovitch in 1920 with the aid of a climate model), numerous amplifying mechanisms are required to account for the magnitude of the changes. The CO₂ concentration during the last major glaciation was about 200 ppm and increased to about 280 ppm prior to human CO₂ contributions. Its concentration in 1999 was about 367 ppm, and it continues

to rise by about 1.5 ppm annually. Much is now understood about the carbon cycle, but knowledge gaps remain. One of them is the role of terrestrial biota, which has been acting as a sink for CO₂, but may not necessarily play that role indefinitely.

The sulfur cycle also has been perturbed by human activities. Cloud droplets and ice crystals form by nucleation



Big baby. Image depicts the ocean surface temperature anomaly known as El Niño.



Creeping up. Atmospheric carbon dioxide concentration measured from Mauna Loa Observatory in Hawaii, by Charles D. Keeling.

1963

Meteorologist Edward Lorenz derives a system of three equations for demonstrating the limits to the predictability of weather, which ultimately leads to the development of chaos theory.

1967

Syukuro Manabe and Richard Wetherald develop the one-dimensional radiative-convective model, including clouds, water vapor, CO₂, and ozone, and show that a doubling of atmospheric CO₂ can warm the planet by about 3 degrees. In 1975, these authors initiate GCM studies of climate change.

1969

Jacob Bjerknes links the Southern Oscillation and El Niño.

1970-74

Paul Crutzen and Harold Johnston identify an ozone-destroying catalytic cycle involving oxides of nitrogen (NO_x). Richard Stolarski and Ralph Cicerone propose another such cycle involving chlorine, and Mario Molina and F. Sherwood Rowland link this cycle to ozone depletion by chlorofluorocarbon (CFC) emissions.

1972

Hiram Levy postulates that reactions with hydroxyl radicals make up the main tropospheric sink for almost all gases emitted into the atmosphere.

1985

The British Antarctic Survey reports a systematic, spring-time reduction of ozone over Halley Bay leading to a 40% drop between 1956 and 1985.

1987

Many countries sign the Montreal Protocol on Substances that Deplete the Ozone Layer, in which signatories agree to controls on the production and use of ozone-destroying materials.

1989

The Earth Radiation Budget Experiment demonstrates that clouds reflect significantly more solar energy than the long-wave radiant heat energy they retain, thus exerting a large cooling effect on the planet.

1990s

Researchers establish the importance of anthropogenic aerosols in potentially offsetting the greenhouse effect by reflecting solar radiation to space.

The global warming trend that began in the 1970s continues, and average surface temperatures reach record values compared with the previous 100 years.

1995

An international team of more than 1000 scientists convenes under the charter of the Intergovernmental Panel on Climate Change and declares: "The balance of evidence suggests a discernible human influence on global climate."

1996

The production of CFCs and some other ozone-depleting chemicals stops in the industrial world.

1997

The Kyoto Protocol calls for legally binding greenhouse gas emission targets for all developed countries.

around submicrometer aerosols consisting of sulfates and organics. That is why aerosols and clouds are strongly linked with climate. Human activities have led to a large increase in these aerosol species. The anthropogenic emission of SO_2 , which converts into sulfate particles in the atmosphere, exceeds that from natural sources, including volcanic emissions and biological "exhalations," by more than a factor of two.

Sulfate particles cool climate directly by scattering sunlight back into space. Sulfates also cool indirectly by nucleating more cloud drops and increasing the brightness (albedo) of clouds. In 1990, Robert Charlson, Joachim Langer, and Henning Rodhe used a global model of the sulfur budget and estimated that the direct cooling effect of sulfates for the past century may have counteracted as much as 20% to 30% of the greenhouse warming. Meanwhile, estimates of cooling from the indirect effect of sulfate range from negligible to offsetting the entire greenhouse forcing (14).

Carbonaceous aerosols from fossil fuel combustion and biomass burning have become another major source of particles. The combination of strong absorption of light by black carbon and scattering by organics and sulfates significantly reduces the amount of solar energy reaching the surface. That raises the specter of regional effects on the hydrological cycle and photosynthesis. One of the main challenges now is to unravel the linkages between aerosols, cloud formation, and climate change. These include the biogenic sources of aerosols such as dimethyl sulfide from plankton and organics from the land; the anthropogenic addition to the cloud condensation nuclei (CCN); the dependence of cloud cover on aerosols and CCN; the response of water vapor and cloudiness to global warming; and the link between solar absorption by black carbon and the hydrological cycle. Unraveling this Gordian knot must start by connecting processes at the microscopic level of aerosol formation with larger scale cloud physical and dynamical processes (16).

We anticipate great advances in our ability to integrate atmospheric phenomena with those of the oceans, land, biosphere, and cryosphere. Global models already have started doing this, but they must be vetted and refined with observations. Atmospheric scientists have a long history of mounting international field experiments, starting with the Global Atmospheric Research Program (conducted by Joachim Kuetner) during the 1970s. Recently, such experiments have begun to integrate physics, chemistry, and dynamics along with data from satellite observations, aircraft, and surface platforms. Only in this way is it possible to begin to grasp the complexity at which atmospheric processes unfold.

One example of this multiscale approach is last year's Indian Ocean Experiment. The study ranged from the scale of particles to that of an entire ocean basin. It tracked how pollutants from South Asia formed a sulfate-organic-soot haze, which spread over the northern Indian Ocean and significantly reduced the solar heating of the oceans. New satellite platforms,

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including NASA's TERRA and the European ENVISAT, also have begun to simultaneously measure several vital chemical, biological, and physical parameters of the atmosphere, ocean, and land.

We should also learn a valuable lesson from history. Aristotle's models of

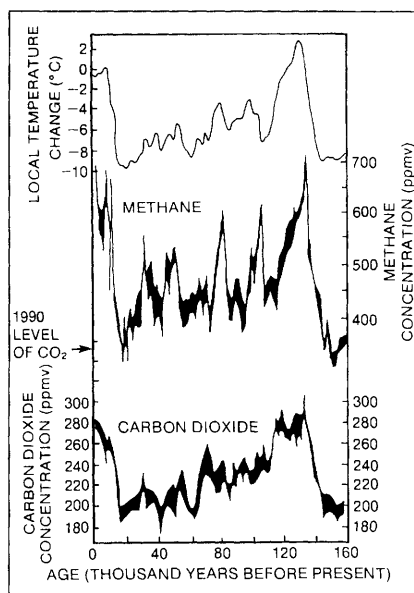
winds and of cloud and rain formation survived nearly 2000 years for lack of observations proving the inadequacy of those models. Due to "prohibitive costs," we too currently lack adequate global-scale observations of such basic atmospheric parameters as the three-dimensional distribution of clouds, aerosols, water vapor, ozone, other chemicals, temperature, and winds. It is our hope that futuristic yet potentially near-term innovations will enable us in the coming decades to float inexpensive microobservers around the globe to gather the data we need to test our ideas, validate our models, and take informed actions.

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Paul J. Crutzen is Professor of Atmospheric Chemistry at the Max Planck Institute for Chemistry in Mainz, Germany. He was a co-recipient of the 1995 Nobel Prize in chemistry for his contributions to the understanding of stratospheric ozone production and destruction.

Veerabhadran Ramanathan is Professor of Atmospheric Sciences at the Scripps Institution of Oceanography, University of California, San Diego, where he directs the Center for Atmospheric Sciences. His research, for which he has received many honors, includes the issues of climate change and human impact on the environment.



Spin cycle. A 160,000-year climate record, derived from antarctic ice core data, showing carbon dioxide, methane, and temperatures changing in phase.