

A

ABRUPT CLIMATE CHANGE

SUMMARY

In 1840, Louis Agassiz published his theory that the Earth had passed through an ice age. As a result of Agassiz's work, the corollary idea that the globe's climate could change dramatically for extended periods entered scientific thinking. Scientists assumed, however, that such change occurred very slowly and smoothly over many millennia. When, in 1922, meteorologist C. E. P. Brooks first proposed that climate can change swiftly, he was largely ignored. During the early 1990s, however, a steady accumulation of data from four main sources strongly supported Brooks's hypothesis. These data suggested that in past epochs the atmosphere went from warm to cool or from cool to warm within decades, perhaps even within a few years.

PROXY EVIDENCE FOR ABRUPT CHANGE

The theory of abrupt change rests on proxy data from ice cores taken from the ice sheets covering Greenland and Antarctica, as well as from tree rings, sediments in oceans and lakes, and coral. In each of these proxies, layers of material are laid down annually and vary in thickness in accordance with annual atmospheric conditions. In tree rings, for instance, wet years foster greater growth in trees, which is reflected in wider rings than those produced during dry years. In addition to such evidence, gases in bubbles trapped in ice reveal the relative abundance of elements at the time they were trapped, which in turn provides clues to atmospheric temperatures at that time.

Taken together, proxy evidence demonstrates not only sudden climate change in past epochs but also frequent change. The most recent of four ice ages lasted from 120,000 to 14,500 years ago. Even during that frigid period, there were twenty-five periods of

abrupt warming, called Dansgaard-Oeschger events, and six extended plunges in temperature, called Heinrich events; in all of them, change took place within decades.

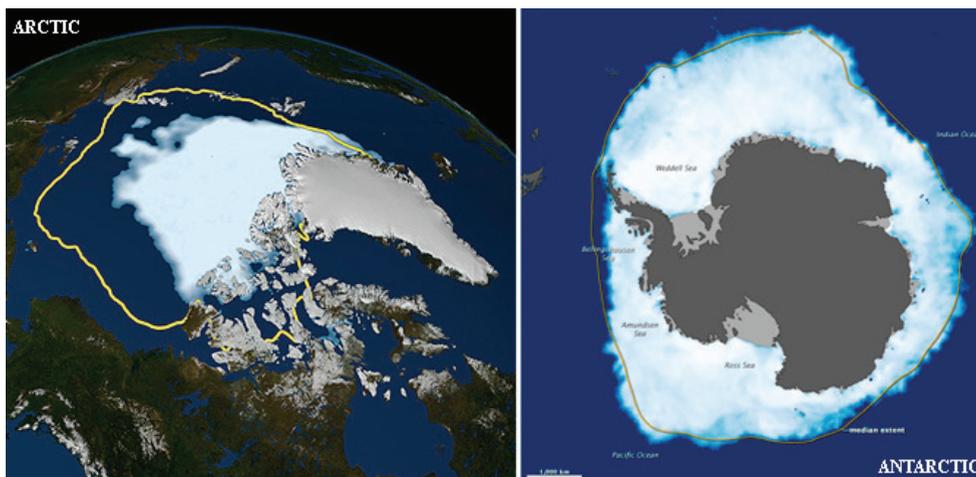
The most studied example of abrupt change is the period known as the Younger Dryas, which began about 12,800 years ago. As the Northern Hemisphere was warming from the ice age, it suddenly relapsed into ice-age temperatures and stayed cold until 11,500 years ago, when temperatures over Greenland rose by 10° Celsius within a decade.

MECHANISMS FOR ABRUPT CHANGE

The United States National Research Council defines abrupt climate change as occurring when the climate system is forced to cross some threshold, triggering a transition to a new state at a rate determined by the climate system itself and faster than the cause.

Mechanisms for such change are poorly understood. It appears that some physical process forces an aspect of the climate system to pass a tipping point—for instance, in the albedo, average cloud cover, or salinity of ocean water. After the tipping point, positive feedback in the system accelerates the warming or cooling trend.

In the case of the Younger Dryas, scientists know that the water of the North Atlantic suddenly became less salty, which slowed or altered the course of the thermohaline cycle. The warm waters of the Gulf Stream no longer flowed north of Iceland and back down along the European coast, causing the continent to relapse to ice-age temperatures. The freshening probably resulted from a sudden outflow of water from a freshwater inland sea, Lake Agassiz, in north-central North America. The physical event that led to this forcing is a point of controversy. Scientists have proposed the breaking of an ice dam



September 2012 witnessed two opposite records concerning sea ice. Two weeks after the Arctic Ocean's ice cap experienced an all-time summertime low for the satellite era (left), Antarctic sea ice reached a record winter maximum extent (right).

after gradual warming or possibly a meteor impact. Forcings for other abrupt changes in past climates include alterations in the salinity of the tropical Atlantic Ocean, evaporation and cloud cover in the South Pacific Ocean, melting of methane clathrates (frozen methane in the ocean beds), and the periodic warming of the South Pacific known as the El Niño-Southern Oscillation (ENSO).

ANTHROPOGENIC GLOBAL WARMING

Scientists worry that increasing levels of greenhouse gases (GHGs) in the atmosphere, much of them released by the burning of fossil fuels, have trapped radiant energy from the Sun in the atmosphere and increased average global temperatures in both the atmosphere and the oceans. This greenhouse effect could lead to abrupt climate change in several ways.

The vast ice sheets in the Arctic and Antarctica have the highest regional albedo on Earth, but they are shrinking rapidly, especially in the Arctic. There, the ice rests primarily on water, which is darker than ice and absorbs more heat. As the ice disappears, there is more exposed ocean surface to absorb solar energy, and the warmed water in turn helps melt the ice faster, creating a positive feedback loop. This melted ice will not affect ocean levels or salinity, but if ice sheets melt off the land of Antarctica or Greenland, ocean levels could rise by dozens of meters within a century, lowering ocean salinity enough

to stall the thermohaline cycle, which could cool Europe rapidly and drastically even while the rest of the world warmed. Should ocean water heat up too much, clathrates could melt and send billions of metric tons of methane into the atmosphere, accelerating global warming further. The augmented thermal energy in the atmosphere is likely to redistribute wind and rainfall patterns, plunging some regions into drought while making others wetter; catastrophic storms, such as hurricanes and tornados, could become more frequent and severe.

CONTEXT

Some scientists argue that the Earth is entering a new geological age, the Anthropocene, because humanity itself now takes part in shaping Earth's overall surface conditions, climate in particular. Particulate pollution (especially soot), waste heat, release of GHGs, water consumption, and alteration of soil and plant cover affect not only the land, water bodies, and atmosphere but also modern civilization. If human effects on the environment trigger abrupt climate change, the onset of icy conditions in the Northern Hemisphere, droughts, superstorms, or rising sea level—all of which are possible according to computer models of climate change—would require radical, swift, and comprehensive measures to adapt or relocate much of Earth's human population. Not only would that be an expensive undertaking, but it

would also mark a shift in the course of human history as profound as the Industrial Revolution.

KEY CONCEPTS

- *albedo*: the fraction of radiation reflected by a surface
- *feedback*: a process in which any change accelerates further changes of the same type (positive feedback) or counteracts itself (negative feedback)
- *greenhouse gases (GHGs)*: atmospheric gases, such as carbon dioxide, water vapor, and methane, that trap heat radiation from Earth's surface by absorbing it and reemitting it
- *proxy*: remnant physical evidence from which past climatic conditions can be inferred
- *thermohaline cycle*: the "great conveyor belt" of ocean currents powered by density gradients created by heat and relative salt content
- *tipping point*: the point at which the transition from one state in a system to another becomes inevitable

—Roger Smith

ACID RAIN AND ACID DEPOSITION

FIELDS OF STUDY

Atmospheric Chemistry; Biochemistry; Environmental Chemistry; Geochemistry; Inorganic Chemistry; Physical Chemistry; Photochemistry; Thermodynamics; Chemical Engineering; Petroleum Refining; Environmental Sciences; Environmental Studies; Waste Management; Physical Sciences; Meteorology; Process Modeling; Fluid Dynamics; Chemical Kinetics; Hydroclimatology; Atmospheric Science; Oceanography; Hydrology; Physical Geography; Ecosystem Management; Ecology; Spectroscopy

SUMMARY

Acid rain is rain that is more acidic than would be natural, as a result of reactions with pollutive, acid-forming gases, such as sulfur dioxide and nitric oxides. Lakes, forests, soils, and human structures in the eastern part of the United States and southeastern Canada have been damaged by acid rain and deposition of sulfuric and nitric acid aerosol on terrestrial objects.

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PRINCIPAL TERMS

- **acid deposition**: the depositing of acidic materials on the ground surface through the action of precipitation
- **acid rain**: rain composed of water having a lower-than-normal pH due to having dissolved and reacted with airborne contaminants to produce acidic materials
- **alkaline**: having a pH greater than 7 due to a lower concentration of hydrogen (H^+) ions than are in neutral water
- **bicarbonate**: a negatively charged ion, as HCO_3^- , that effectively neutralizes excess hydrogen ions in natural waters, reducing acidity
- **cap and trade legislation**: legislation that places limits on the emission of acid-producing materials, such as sulfur dioxide, while allowing emitters of excess amounts to purchase and utilize the unused allowances of those whose emissions are below the legislated limit
- **limestone**: a rock containing calcium carbonate that reacts readily with acid rain and tends to

neutralize it, being chemically eroded in the process

- **neutralization:** the adjustment of the concentration of hydrogen ions in solution in order to achieve neutral pH
- **nitric acid:** an acid formed in rain from nitric oxide gases in the air
- **nitric oxide gases:** gases formed by a combination of nitrogen and oxygen, particularly nitrogen dioxide and nitric oxide
- **pH:** a measure of the hydrogen ion concentration, which determines the acidity of a solution; the lower the pH, the greater the concentration of hydrogen ions and the more acidic the solution
- **sulfur dioxide:** a gas whose molecules consist of one sulfur atom and two oxygen atoms, formed by the combustion of sulfur in the presence of oxygen
- **sulfuric acid:** an acid formed as the primary component of acid rain by reaction of sulfur dioxide gas with liquid water in the atmosphere

DEFINITION AND CAUSE

Acid rain is rain that is more acidic than it would be normally, usually because it has reacted with acid-forming pollutant gases. The acidity of rain is measured in pH units, which are the negative logarithmic values of the concentrations of hydrogen ions in solution. Pure water, which is neutral, has a pH of 7, reflecting the natural concentration of hydrogen ions in pure water of 1×10^{-7} moles per liter. Any solution with a pH greater than 7 is basic, or alkaline, and any solution with a pH less than 7 is acidic. The lower the pH, the more hydrogen ions there are and the more acidic the solution is.

The natural acidity of rain is determined by its reaction with carbon dioxide gas in the atmosphere, a reaction that produces carbonic acid. Carbonic acid partly dissociates to produce hydrogen ions and bicarbonate ions. As a result of this reaction, pure rain water is moderately acidic, with a pH of 5.7. Any rain with a pH less than 5.7 is called “acid rain” and has reacted with acid-forming atmospheric gases other than carbon dioxide. Reaction of water with sulfur dioxide, for example, produces sulfuric acid in rain, and reaction of water with nitrogen dioxide produces nitric acid in rain. In some cases, acid rain has been observed to have a pH value as low as 2.4, which is as acidic as vinegar.

In addition to acid rain, there is “dry deposition,” which occurs without rain and deposits acidic nitrate and sulfate particles and sulfuric and nitric acid aerosols from the atmosphere. The acidic particles are trapped by vegetation or settle out, and the gases are taken up by vegetation. “Acid deposition” usually refers to dry deposition of acids.

Acid rain was first recognized in Scandinavia in the early 1950s. It was discovered that acid rain (with a pH from 4 to 5) came from winter air masses that were carrying pollution into Scandinavia from industrial areas in Central and Western Europe. Rain became more acidic over the next twenty years, and the area of Europe receiving acidic rains increased. By the mid-1970s, most of northwestern Europe was receiving acid rain with a pH of less than 4.6. As a result of the discovery of acid rain in Europe, scientists began measuring the acidity of North American rain. Initially, around 1960, acid rain was concentrated in a bull’s-eye-shaped area over New York, Pennsylvania, and New England. By 1980, however, most of the United States east of the Mississippi River and southeastern Canada was receiving acid rain (pH less than 5.0), and the central bull’s-eye was receiving very acidic rain, having a pH less than 4.2. The greatest increase in the acidity of rain was in the southeastern United States.

The primary cause of acidity in U.S. and European rains is sulfuric acid, which comes from pollutant sulfur dioxide gas produced by the burning of sulfur-containing fossil fuels, particularly coal, but also oil and gas. In the United States, much of the sulfur dioxide gas is produced in the industrial area of the Midwest. However, sulfur dioxide gas and the resulting sulfuric acid can be transported for a distance of 800 kilometers to the northeast by the prevailing winds in the atmosphere before precipitating as acid rain in the northeastern United States and southeastern Canada. To reduce the acidity of rain in the East, then, the emissions of sulfur dioxide gas in the Midwest would have to be reduced. Another source of sulfur dioxide gas is smelters that process ores, such as that in Sudbury, Ontario, located north of Lake Huron in Canada, which is one of the largest sources of sulfur emissions in the world. This smelter’s high exhaust stack spreads sulfuric acid aerosols over an extensive area hundreds of kilometers downwind. The original intent of building high exhaust stacks was to reduce local air pollution, but the net effect

has been to spread the pollution over much larger areas. Acid rains are even found in Alaska, where sulfuric acid particles have been transported from the contiguous United States.

Nitric acid is a secondary cause of acid rain (contributing about 30 percent of the acidity), but it is one that is increasing. Nitric acid comes from the nitrogen oxide gases, nitrogen dioxide, and nitric oxide, which are produced by the burning of fossil fuels. In contrast to sulfur dioxide, 40 percent of the pollutive nitrogen oxide gas comes from vehicles and most of the remainder from power and heating. The production of nitrogen oxides therefore tends to be concentrated in urban areas. Nitric acid is an important component of acid rain in Los Angeles, for example, because air pollution from vehicle exhaust tends to become trapped in this area.

Some acid rain results from natural causes. Reduced sulfur gases, such as hydrogen sulfide and dimethyl sulfide, are produced by organic matter decay and converted to sulfur dioxide and sulfuric acid in the atmosphere. This process results in naturally acid rain. Volcanoes are another natural source of sulfur dioxide gas. Nevertheless, about 75 percent of the sulfur dioxide gas produced in the United States comes from the burning of fossil fuels. Naturally acid rain (with a pH less than 5.5) is uncommon, falling chiefly in remote areas such as the Amazon basin and some oceanic areas.

There are natural factors that work to reduce or neutralize the acidity of rain in certain areas. Windblown dust, particularly that containing limestone particles, tends to make rains in arid areas of the western United States less acidic by reacting with the acid to produce a rainwater solution with a pH of 6 or more. In addition, the presence of ammonia gas produced in agricultural areas by animal waste, fertilizers, and the decomposition of organic matter will reduce or counteract the acidity of rain on a local scale.

EFFECTS OF ACID RAIN AND ACID DEPOSITION

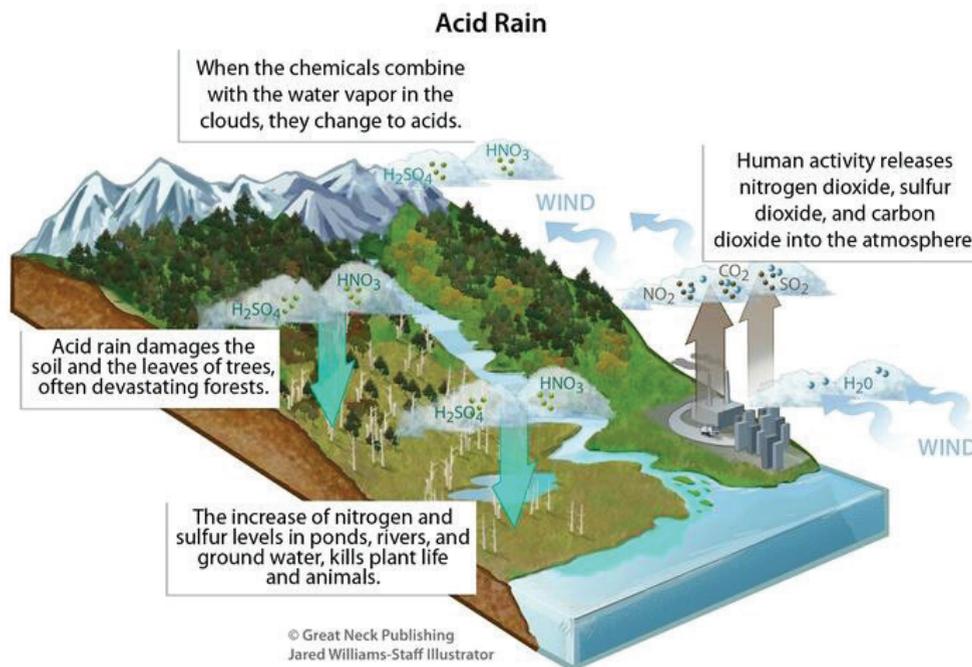
The detrimental effects of dry deposition and acid rain include the corrosion and chemical erosion of structures and buildings made of susceptible materials, changes in soil characteristics, increases in the acidity of lakes, and other biological effects, particularly in high-altitude forests. The corrosive effects of airborne acids are particularly obvious on limestone,

a rock composed of calcium carbonate, which reacts easily with acid rain. In many New England cemeteries, tombstones made of marble, a form of limestone, have been badly corroded, although older tombstones made of slate, which is less affected by acid rain, are intact. Limestone components of buildings and other structures are similarly corroded.

The effect of acid rain on soils depends on their composition. Alkaline soils that contain limestone have the ability to neutralize acid rain. Even in soils that do not contain limestone, several processes operate to neutralize acid rain, though such processes invariably alter the chemical nature of the soil. Cation exchange occurs, whereby hydrogen ions from the rainwater are exchanged for metal ions, such as calcium or magnesium, on the surface of clays and other minerals. This exchange removes excess hydrogen ions from soil solutions, rendering them less acidic. Another neutralization process involves the release of soil aluminum into solution and the accompanying uptake of hydrogen ions. This process occurs by dissolution of aluminum bound to clays and organic compounds. Frozen soils and sandy soils containing mostly quartz, which does not react with acid rain, have little ability to neutralize acid rain.

Lakes in certain areas have become acidic (with a pH less than 5) from the deposition of acid rain. Lakes in granitic terrain are most affected by acid rain because the surrounding bedrock has little or no ability to react with or neutralize the excess hydrogen ions in the water. Areas with many acid lakes include the Adirondack Mountains in New York, the Pocono Mountains in Pennsylvania, the Upper Peninsula of Michigan, Ontario, Nova Scotia, and Scandinavia. Generally, the deposition of highly acidic rain having a pH less than 4.6 over a long period of time is required. The effect is enhanced in bodies of water that are maintained by watershed drainage rather than by freshwater springs.

Lake waters that have a tendency to become acidified initially have little ability to neutralize acid rain because they are low in carbonate and bicarbonate ions, which come predominantly from limestone. Such lakes are described as being poorly buffered. (Buffering is the resistance to changes in pH upon the addition of acid or base.) The soil in the drainage area surrounding acid lakes does not neutralize acid rain adequately before it reaches the lake because of a lack of limestone and clay minerals or because



This illustration shows the effects of acid rain on the environment.

the soil cover is thin or lacking altogether. In addition, some lakes, although not usually acidic, may have periods of elevated acidity due to the runoff of snowmelt, which collects acid precipitation stored in the snow. This runoff gives a sudden large pulse of highly acidic water to the lake. In certain areas, such as Florida, acid lakes result partly due to causes other than acid rain, such as the presence of organic acids produced by the decay of vegetation in poorly drained areas and nitric acid formed from nitrate-based fertilizer runoff. The gradual acidification of lakes results in the death of fish populations because of reproductive failure, as well as other changes in the organisms living in the lake. A reduction in the number of species occurs at all levels of the food chain. In some cases, snowmelt acidity has been identified as the cause of a massive, instantaneous fish kill in lakes.

Rivers are also known to become acidic. Eastern U.S. rivers show high concentrations of sulfate and a low pH in cases where the soil cannot neutralize the acid rain it receives. Certain acid rivers are caused by acidic drainage from mine dumps rather than by acid rain. Acid rivers rich in organic matter are found

in the eastern United States coastal plain and in the Amazon basin. These rivers have naturally high concentrations of dissolved organic acids.

Acid rain and acid deposition are implicated in the decline and death of certain forests, particularly evergreen forests at high elevations. These forests receive very acidic precipitation from the accumulation of clouds at the mountaintops. It is thought that acid rain does not actually kill the forests but rather provides a stress that causes them to become less resistant and die from other causes. The actual stress provided by acid rain is still being studied. Possible stresses include loss of nutrients from soil and leaves through leaching, destruction of beneficial soil microorganisms, and increased susceptibility to frost damage during winter.

Efforts have been made to reduce the acidity of rain, particularly by controlling sulfur emissions. Power plants have been required to reduce the sulfur content of coal that they burn, thus lowering the amount of sulfur dioxide that is produced. Sulfate concentrations in rain in the northeastern United States have been reduced by this method. Nitrogen oxide emissions from cars have also been reduced

through stricter emissions controls and improved engineering design for more efficient combustion. In some cases, acid lakes have been treated with limestone to temporarily neutralize their acidity, but the only permanent solution is a reduction in the acidity of the rain that they receive.

STUDY OF ACID RAIN AND ACID DEPOSITION

The acidity of rain can be measured directly by an electronic device called a pH meter. A pair of electrodes is inserted into a solution, and the electrical potential, or voltage, is measured between them. This voltage is directly related to the concentration of hydrogen ions in the solution—that is, to the acidity of the solution. To monitor and measure the acidity of rainwater, networks have been constructed to collect rain samples over large geographical areas. The acidity of rainwater over the course of the entire year must be measured because pH varies between rainfalls, both seasonally and according to whether the air masses that produce the rain have passed over significant sources of pollution. The pH of rainwater and other forms of precipitation is also measured over a period of years.

In addition to the concentration of hydrogen ions, the concentration of other ions, such as sulfate from sulfuric acid and nitrate from nitric acid, is measured in the rainwater samples. Such measurements give evidence of the source of the acidity—that is, which proportion is attributable to sulfuric acid and which to nitric acid. The pH levels of samples collected over a large geographical area are plotted on a map, and contours are drawn through equal values of the pH. Such maps show which areas are receiving the most acid rain. The amount of sulfate and nitrate being deposited by rain is also plotted separately. Meteorologists also use information about a storm system's path as it moves across the country. Such atmospheric systems transport pollutive gases from one area to another. Combining deposition patterns on maps with information about the path followed by a storm shows where the gas residues in rainwater may be coming from and suggests sources of the acidity.

Computers have been used to predict where acid rain will fall and how acidic it will be, given the sources and amounts of sulfur and nitrogen emissions, particularly from power plants and smelters, and the weather patterns. Predictions of this type require a detailed knowledge of the atmospheric

chemistry by which sulfur dioxide is converted to sulfuric acid and the oxides of nitrogen are converted to nitric acid. This type of modeling is necessary to predict how much reduction in the acidity of rain in a distant area will result from a given reduction in a power plant sulfur source, for example.

The effects of acidity on soils have been the subject of study for many years. Laboratory experiments can demonstrate how soil clays and other minerals react to acid rain, including which chemical species are taken up and which are released. In addition, soil solutions and minerals are collected and analyzed from actual field areas affected by acid rain. Ideally, such an analysis should be carried out over a period of time to determine whether any changes in the soil solution chemistry are occurring. From a knowledge of the soil chemistry, it is possible to predict how long a soil can receive acid rain before it loses particular nutrients or the ability to neutralize the excess acidity.

Measuring the acidity and chemical composition of lakes in various areas over long periods and sampling their fish populations and other biota enables scientists to see increases in lake acidity and to correlate the increases with changes in the populations of affected species. In some areas, lakes have been artificially acidified so that the changes in their chemistry and biological populations can be observed. Apparently, acidic lake water inhibits reproduction in fish and other creatures, in addition to destroying the organisms that they use for food. Computer models of acid rain falling on susceptible drainage areas of lakes are made in order to predict how the drainage area reacts to acid rain and how much reduction in acid rain would be necessary to lower the acidity of the lake to the point where it would support fish. In badly affected areas such as the Adirondacks, it may be necessary to reduce the acidity by half.

To study forest decline, surveys of present forest conditions are compared with historical records for the same areas. For example, in high-elevation areas in New England and the Adirondacks, more than half of the red spruce died between 1965 and 1990. Tree rings, which record annual growth, show reduced growth in certain forests. It is known that acid rain causes changes in the soil, such as the release of aluminum, which is toxic to root tissues and so prevents the uptake of essential nutrients. In addition, acid rain causes the loss of certain nutrients from the soil, such as sodium, calcium, and magnesium.

Another effect of acid rain is the reduction of the numbers of microorganisms in the soil. Yet, because acid rain from nitric acid contains nitrogen, a plant nutrient, it may fertilize the soil if there is a deficiency of soil nitrogen. One problem in studying forests receiving acid rain is determining which of the many changes occurring are contributing most to forest damage. It is often difficult to distinguish between the stresses of acid rain and other stresses, such as those caused by drought, cold, and insects. Field studies in this area may involve artificial acidification of forest environments in order to determine which mechanisms are important.

—Elizabeth K. Berner

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AEROSOL POLLUTANTS

FIELDS OF STUDY

Physical Chemistry; Geochemistry

SUMMARY

The effects of aerosol pollutants have been debated for a long time. Release of volcanic dust from the 1783 eruption of a volcanic fissure in Iceland seemed to have been related to an unusually cool summer in France the same year. In 1883, volcanic dust from the explosion of Krakatoa in the East Indies dimmed the sunlight for months, as had the 1815 eruption of Tambora. Some scientists perceived a pattern of temporary cooling from such events. Others asked if pollutants should be expected to warm, rather than cool, the atmosphere.

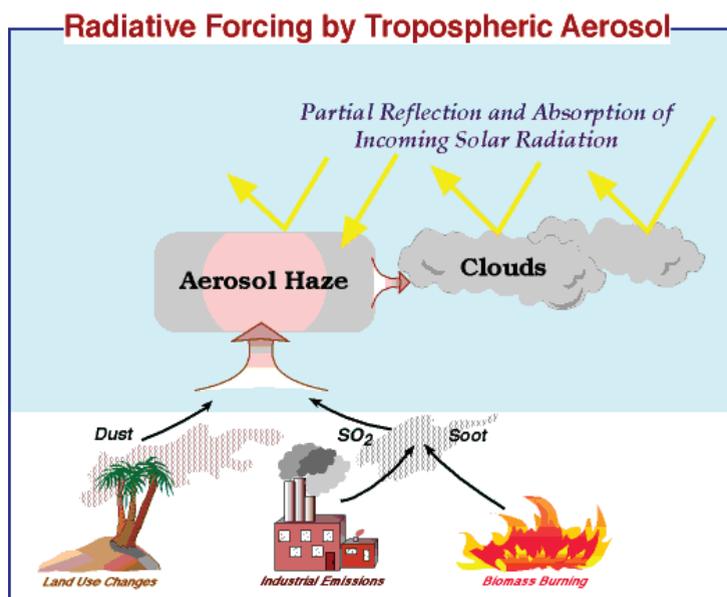
PRINCIPAL TERMS

- **cloud condensation nuclei:** atmospheric particles such as dust that can form the centers of water droplets, increasing cloud cover

- **dust Veil Index:** a numerical index that quantifies the impact of a volcanic eruption's release of dust and aerosols
- **global dimming:** the effect produced when clouds reflect the Sun's rays back to space
- **stratosphere:** part of the atmosphere just above the troposphere that can hold large amounts of aerosols produced by volcanic eruptions for many months
- **troposphere:** location in the lower atmosphere where the majority of aerosols form a thin haze before being washed out of the air by rain

CHARACTERISTICS OF AEROSOLS

Aerosols are minute airborne solid or liquid particles suspended in the atmosphere, typically measuring between 0.01 and 10 microns and either natural or anthropogenic in origin. Normally, most aerosols rise to form a thin haze in the troposphere; rain washes these out within about a week's time. Some aerosols, however, are found in the higher stratosphere, where



Aerosols can both reflect and absorb solar radiation, making their role in the greenhouse effect particularly complex.

it does not rain. They can remain in this atmospheric layer for months. Aerosols may influence climate either directly, through scattering and absorbing radiation, or indirectly, by acting as cloud condensation nuclei or by modifying the optical properties and lifetimes of clouds.

Natural aerosol sources include salt particles from sea spray; clay particles from the weathering of rocks; volcanic emissions of sulfur dioxide, which oxidizes to form sulfuric acid molecules and sulfate salts; and desert dust. Anthropogenic (human-produced) aerosol sources include industrial pollutants such as sulfates, from combustion of oil and coal; smoke from large-scale burning of biomass, such as occurs in slash-and-burn clearing of tropical forests; and pollution from naval vessels' smokestacks and the transportation sector in general.

On windy days, bubbles created by breaking waves eject salt into the air when they burst, forming aerosols. Salt aerosols scatter sunlight, lessening the amount of energy that reaches Earth's surface which acts to cool the climate. The interaction of sea salt with clouds also causes cooling. The resulting overall 'whitening' of the Earth further reduces the amount of sunlight that can reach the ground. Oceans cover over 70 percent of Earth's surface, and sea salt is a

major source of aerosols in areas far distant from land.

Wind also helps form aerosols over land. Particles carried by the wind abrade the surfaces of rock and other landforms. This action wears down rocks and other surfaces progressively over time, converting them eventually into fine dust particles of stone and other materials. When these particles are incorporated into the air, they too form aerosols.

Following major volcanic eruptions, sulfur dioxide gas vented during the eruptions is converted into sulfuric acid droplets. These droplets form an aerosol layer in the stratosphere. Winds in the stratosphere scatter the aerosols over the entire globe, where they may remain for about two years. Because they reflect sunlight, these aerosols also reduce the amount of energy that reaches the troposphere and the Earth's surface, exerting a cooling influence.

Another significant natural aerosol is desert dust. "Veils" of dust stream off deserts in Asia and Africa, and have also been observed on the American continents. These particles typically fall out of the atmosphere after a short flight, but intense dust storms often blow them to altitudes of 4,500 meters or higher, allowing them to reach great distances from their source. Since the dust is made up of minerals,

the particles both absorb and scatter sunlight. Absorption warms the layer of the atmosphere where they are located, possibly inhibiting the formation of storm clouds and contributing to desertification.

EARLY SPECULATION ABOUT AEROSOLS

Long before there was much interest in aerosols as a factor in climate change or any equipment capable of adequately analyzing aerosol data, a few individuals speculated about a possible aerosol-climate connection. The first man credited with reporting these ideas was Jacques Antoine Morgue de Montredon (1734 – 1818), a French naturalist who in 1783 documented the eight-month-long Laki eruption in southern Iceland. The eruption caused the grass to die. Three-quarters of the region's livestock and one-quarter of its people starved to death. For months, a haze hovered over western Europe. When Benjamin Franklin was visiting in France in 1783, he experienced an unseasonably cold summer and speculated that the Laki volcanic "fog" had noticeably dimmed the sunlight.

A century later, in 1883, the eruption of the Indonesian volcano Krakatoa (Krakatau) sent up a veil of volcanic dust that reduced sunlight globally for months. Scientists were unable to determine what effect the eruption might have had on the average global temperature, but scientists thereafter acknowledged volcanoes as a possible natural influence on Earth's climate.

A few scientists who examined temperatures after major volcanic eruptions between 1880 and 1910 perceived a pattern of temporary cooling. Only later would older records reveal that the 1815 eruption of Tambora in Indonesia had affected the climate more severely than had the eruption of Krakatoa. Speculation led some to ask if volcanic eruptions had precipitated ice ages or had cooled the Earth to the extent that dinosaurs became extinct.

EARLY TWENTIETH CENTURY AEROSOL RESEARCH

Throughout the first half of the twentieth century, it was known that volcanic aerosols could affect climate. As a result, some scientists suspected that other kinds of particles could have similar climatic effects. Physics theory seemed to support the notion that these particles should scatter radiation from the Sun back into space, thereby cooling Earth's overall

climate. These ideas remained largely speculative, though some researchers began to focus on the possibility that human activity might be a major source of atmospheric particles.

In the 1950's, nuclear bomb tests provided improved data on aerosol behavior in the stratosphere. It was determined that stratospheric dust would persist for some years, but would stay in one hemisphere. Research in the early 1960's indicated that large volcanic eruptions lowered average annual temperatures. Some researchers, however, deemed those results enigmatic, since temperatures had also decreased during a period of few eruptions. Meteorologists acknowledged that other small, airborne particles could influence climate, but throughout the first half of the century, speculation fell short of conclusion.

Gradually, scientists shifted their focus to anthropogenic atmospheric particles. Measurements by ships between 1913 and 1929 noted that sea air showed an extended decrease in conductivity, apparently caused by smoke and gases from the stacks of ships and possibly from industry on land. Even in 1953, however, scientists were uncertain about the significance of the pollution.

During the 1950's, some scientists asked whether aerosols might affect climate by helping form clouds. Since particulate matter is essential for providing a nuclear surface for water droplets to condense around, the notion of seeding clouds with silver iodide smoke to make rain became widespread. By this time, aerosol science was just coming into its own as an independent field of study, having been given impetus by the concern that disease-carrying aerosols and poisonous gas could be employed with lethal effect. Public concern over urban smog also fueled studies by aerosol experts. By and large, however, scientists avoided the study of cloud formation. Field testing often produced contradictory results and was extremely expensive, and many researchers believed that the effects of aerosols on clouds were too complex to comprehend.

AEROSOL RESEARCH IN THE LATER TWENTIETH CENTURY

By the early 1960's, the scientific community was beginning to pay more attention to the possibility that human activities influence clouds. It was predicted that jet airplane contrails would spread, thin, and become indistinguishable from cirrus clouds, and this

was borne out by observation. The apparent ability of aircraft to create cirrus clouds suggested the possibility that they might be causing climate changes along major air routes. Others questioned the possibility of anthropogenic activity as the source of pollution settling on polar ice caps. At the time, the theory was not given much credence.

Around 1970, the British meteorologist Hubert Horace Lamb (1913–1997) devised the Dust Veil Index, establishing a connection between atmospheric dust and lower temperatures. While scientific studies at this time did not yet find strong evidence for an increase in global turbidity, they did document regional hazes that spread in a radius of up to one thousand kilometers or more from industrial centers. The scientific debate shifted from the existence of anthropogenic dust to the effects of that dust. It remained a subject of controversy whether and under what circumstances dust would cool or heat the climate, especially after a spacecraft on Mars in 1971 found that a large dust storm had caused substantial warming of the Martian atmosphere.

Deadly droughts in Africa and South Asia in 1973 caused public concern about climate change, but it was not confirmed that sulfate pollution had contributed to the Sahel drought until the end of the century. Scientific publications in the mid- to late 1970's discussed warming or cooling effects without reaching accord, although a majority felt that greenhouse warming would dominate. At this time, only a few researchers noted that aerosol pollution might cancel out some greenhouse warming and thus temporarily mask its effects. Others denied that industrial pollution could mitigate the enhanced greenhouse effect caused by carbon dioxide (CO₂) emissions.

The 1980's brought the realization that additional factors contributed to climate and climate change. For example, climate scientists generally treated aerosols as a globally uniform background, largely of natural origin, when in fact different aerosol properties were obtained in different regions based on relative humidity. Many questions remained.

By 1990, it was acknowledged that from one-fourth to one-half of all tropospheric aerosol particles were anthropogenic. These included industrial soot and sulfates, smoke from forest-clearing fires, and dust from overgrazed or semiarid land turned to agriculture. Impressive advances in laboratory instrumentation

made possible much more sophisticated satellite observations, greatly increasing the resolution of climate models. A key paper establishing the net effect of aerosols on Earth's heat balance, published in the early 1990's, concluded that radiation scattering due to anthropogenic sulfate emissions was counterbalancing CO₂-related greenhouse warming in the Northern Hemisphere.

It became apparent that earlier climate projections might be erroneous, because they had not factored in sulfate aerosol increases. Climatologists redoubled their efforts to produce accurate models and projections of Earth's climate. In 1995, for the first time, new results that took into account aerosol influence yielded a consistent and plausible picture of twentieth century climate. According to this picture, industrial pollution had temporarily depressed Northern Hemisphere temperatures around the mid-century. A 2008 study found that black carbon aerosols had exerted a much greater warming effect than had been earlier estimated, because the combined effects of black carbon with sulfate aerosols had not been taken into account. It seemed clear that reducing sooty emissions would both delay global warming and benefit public health.

CONTEXT

A number of aerosol specialists have questioned whether they have underestimated the cooling effect of aerosols. If they had, they would have underestimated those aerosols' restraint of greenhouse warming, significantly underestimating the extent of global warming in the absence of anthropogenic aerosol pollution. Much uncertainty remains, and each new study introduces new complexities. It seems clear that reducing sooty emissions would both delay global warming and benefit public health, yet nagging questions remain: Since aerosols and clouds, unlike gases, are not distributed evenly throughout the atmosphere, uniform samples cannot be obtained. Further, the properties of clouds and aerosols are incompletely understood, and scientists are only beginning to understand some of the interactions that take place between aerosols, clouds, and climate. Thus, these interactions have not yet been fully incorporated into climate models.

—Victoria Price

FURTHER READING

- Le Quéré, Corinne and Saltzman, Eris S., eds. *Surface Ocean-Lower Atmosphere Processes* John Wiley & Sons, 2013. This 187th volume of the Geophysical Monograph series provides a clear and documented description of processes contributing to aerosol formation at the surface of Earth's oceans.
- Seinfeld, John H. and Pandis, Spyros N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* 3rd ed. John Wiley & Sons, 2016. Presents a comprehensive historical perspective and overview of the chemistry and physics of the atmosphere, with multiple chapters covering aerosols and their effects.
- Tanvir, Islam, Hu, Yongxiang, Kokhanovsky, Alexander and Wang, Jun, eds. *Remote Sensing of*

Aerosols, Clouds and Precipitation Elsevier, 2017. Describes the methods, theoretical foundations and applications of satellite-based monitoring of aerosols, clouds and precipitation events occurring in Earth's atmosphere.

- Wang, Yuan. *Aerosol-Cloud Interactions from Urban, Regional and Global Scales* Springer Theses/Springer, 2015. Written for a highly technical, Ph.D-level audience, this is an advanced study examining the aerosol-cloud-precipitation interaction in a quantitative manner. A significant contribution is made to coordinating regional and global climate prediction models, based on radiative forcing by atmospheric aerosols.

AIR POLLUTION**FIELDS OF STUDY**

Atmospheric Science; Atmospheric Chemistry; Photochemistry; Environmental Chemistry; Thermodynamics; Chemical Engineering; Petroleum Refining; Engineering; Environmental Sciences; Environmental Studies; Waste Management; Meteorology; Climate Modeling; Process Modeling; Fluid Dynamics; Hydroclimatology; Hydrometeorology; Bioclimatology; Physical Geography; Ecosystem Management; Ecology; Toxicology; Pathology; Spectroscopy

SUMMARY

Air pollution is generated from both natural and anthropogenic sources. Natural sources include gases, particulate matter from volcanoes and decomposing organic matter, pollen from plants, and windblown dust. Anthropogenic sources include industrial and automobile emissions and airborne particles associated with human-induced abrasion.

PRINCIPAL TERMS

- **acid rain:** precipitation having elevated levels of acidity relative to pure water
- **atmosphere:** the layer of mixed gases that surrounds Earth

- **carbon dioxide:** CO₂, one of many minor gases that are natural components of the atmosphere; the product of the complete oxidation of carbon
- **greenhouse effect:** the environmental process that results when heat energy is absorbed and retained in the atmosphere by various gases and is not radiated out into space
- **inversion:** an unusual atmospheric condition in which temperature increases with altitude
- **off-gassing:** the spontaneous emission of entrained or entrapped gases from within natural and artificial sources
- **oxides of nitrogen:** several gases that are formed when molecular nitrogen is heated with air during combustion, primarily NO and NO₂
- **oxides of sulfur:** gases formed when fuels containing sulfur are burned, primarily SO₂
- **ozone:** a highly reactive compound composed of three atoms of oxygen, as O₃
- **photochemical oxidants:** pollutants formed in air by primary pollutants undergoing a complex series of reactions driven by light energy
- **photochemical reaction:** a type of chemical reaction that can occur in polluted air driven by the interaction of sunlight with various pollutant gases

EARTH'S ATMOSPHERE

Air pollution results from the unusual addition of gases, solids, and liquids to the atmosphere. The concentration of pollutants depends on prevailing atmospheric conditions as well as emission rates. Once pollutants are put into the atmosphere, it is impossible to control them to any significant degree. Thus emissions at the local level contribute to regional and global air pollution problems, such as smog and photochemical oxidants, acid precipitation, the depletion of the ozone layer, and global warming associated with the intensification of the greenhouse effect. Although there are many air pollutants, the major ones are usually associated with burning, particularly the burning of fossil fuels and oil-carbon dioxide based products. They are generally unburned hydrocarbons, oxides of sulfur and nitrogen, carbon monoxide, various photochemical oxidants and reactive compounds, and particulate matter from many different sources.

The atmosphere is a mixture of gases, aerosols, and particulate matter surrounding Earth. The concentration of some of the gases in clean air is fairly constant both spatially and temporally. Consequently, these gases are referred to as stable or permanent gases. Nitrogen and oxygen, the two most abundant permanent gases, account for 78 percent and 21 percent of the total atmosphere by volume, respectively. Gases that experience noticeable temporal and spatial variations are termed variable gases. The two most abundant of these are water vapor and carbon dioxide. The average concentration of carbon dioxide is about 0.034 percent. It varies seasonally in response to the growth cycle of plants, daily in response to plant photosynthesis, and spatially in response to the burning of fossil fuels. Water vapor is also highly variable. Some variable gases have natural origins and tend to have relatively high concentrations in urban areas. They are methane, carbon monoxide, sulfur dioxide, nitrogen dioxide, ozone, ammonia, and hydrogen sulfide.

The atmosphere is stratified according to its vertical temperature gradient. From the ground surface up, the major layers are the troposphere, the stratosphere, the mesosphere, and the thermosphere. The troposphere contains the bulk of atmospheric gases and, under normal conditions, is characterized by a fairly uniform temperature decline from the surface

upward. The uppermost limit of the troposphere is called the tropopause, a transition zone between the troposphere and stratosphere where temperatures stabilize with increasing altitude. The troposphere extends up to about 10 kilometers. The next layer encountered is the stratosphere, which extends from about 12.5 kilometers up to about 45 kilometers above the surface. In its lower layer, the temperature gradient is somewhat stable. At an elevation of about 30 kilometers, however, the temperature starts to increase. Located within the stratosphere about 24 to 32 kilometers above the Earth's surface is a zone with a relatively high concentration of ozone, a triatomic form of oxygen. This zone is called the ozone layer. It is important because the ozone absorbs most of the incoming ultraviolet rays emitted by the sun, preventing them from reaching the surface where they would have harmful effects on plant and animal life.

The two uppermost layers, the mesosphere and the thermosphere, have a distinctive temperature gradient. In the mesosphere, temperatures decline steadily with altitude, a condition that continues until its transition zone with the thermosphere, called the mesopause, is reached. At latitudes of 50 degrees north and higher, mesospheric clouds known as noctilucent clouds are sometimes seen during summer. These clouds may be anthropogenic in origin. The last layer, the thermosphere, slowly gives way to outer space and has no defined upper limit.



Smog blankets the Chinese countryside north of Beijing on a late November day. (Sean O'Keefe)

ATMOSPHERIC INVERSIONS AND SMOG

Vertical and horizontal mixing of air is necessary to dilute pollutants in the atmosphere. Under normal conditions, temperatures decline with altitude in the troposphere. This decline in temperature with altitude is referred to as the thermal or environmental lapse rate. The warmer air near the surface rises, mixes with the air above it, and is dispersed upward by winds. This dilution process is important in reducing the concentration of pollution near the surface. Conversely, the vertical mixing of air is inhibited when the temperature profile in the troposphere inverts, developing one type of atmospheric inversion: a temperature or thermal inversion. When an inversion exists, a layer of warmer air becomes sandwiched between two layers of cooler air above and below, and the warmer, less dense air does not rise as it would normally. Pollutants can then accumulate below the warmer air as vertical mixing is prevented.

Conditions for temperature inversions develop when the Earth readily radiates heat energy from its surface on clear nights or when air subsides and warms adiabatically from compression. On cool, clear nights, the Earth readily radiates heat energy to space, cooling the surface. Air near the surface is, in turn, cooled by conduction, while the air above it is still relatively warm. This condition is referred to as a radiation inversion. Radiation inversions are common during autumn and are usually short-lived, as the rising sun in the morning heats the air near the surface, causing the inversion to dissipate as the day advances. Less frequent but more persistent subsidence-type inversions can occur when cooler air subsides in high-pressure systems or in valleys, as cooler, denser air descends along adjacent mountain slopes. Subsidence inversion episodes may last for days, allowing pollutants to concentrate to excessive levels, causing eye irritation, respiratory distress, reduced visibility, corrosion of materials, and soiling of clothes.

The atmosphere has inherent self-cleansing mechanisms. Pollutants are removed from the atmosphere through fallout due to gravitational settling, through rainout in condensation and precipitation processes, through washout as waterdrops and snowflakes accumulate pollutants as they fall to Earth, and through chemical conversion. Solar radiation, winds, and atmospheric moisture are important meteorological factors in these removal processes.

Chemical reactions between two or more substances in the atmosphere produce secondary pollutants, which are those created from other pollutants that have been released directly into the atmosphere from identifiable sources. Smog is a product of such reactions. Stability in the atmosphere that accompanies inversions provides favorable conditions for smog to develop. Smog is produced by chemical and photochemical reactions involving primarily sulfur oxides, hydrocarbons, and oxides of nitrogen. Smog that is characterized by sulfur oxides is called sulfurous smog and is associated with the burning of fuels having relatively high sulfur content. This type of smog is common in undeveloped countries. Photochemical smog develops when oxides of nitrogen and various hydrocarbons undergo photochemical reactions to produce ozone and other chemical oxidizers. Sunlight promotes the reactions, and automobile exhaust is a primary source of nitrogen oxides. This is the type of smog typically encountered in large cities and urban centers such as Los Angeles and Mexico City. In November 2014, the United States Environmental Protection Agency announced tightened restrictions on smog levels, lowering the acceptable level from 75 parts per billion to 65 to 70 parts per billion. According to the agency, a standard of 70 parts per billion would greatly improve the quality of life in high-pollution areas, preventing 1,400 asthma-related emergency room visits and 750 premature deaths.

ACID PRECIPITATION

While smog is a relatively localized phenomenon closely associated with urban areas, acid precipitation is a more widespread phenomenon. Its effects are observed in national parks, agricultural regions, forested areas, and lakes and other bodies of water as well as in urban centers. Acid rain develops when oxides of sulfur or nitrogen combine with water vapor in the atmosphere to form sulfuric and nitric acids that fall back to Earth in precipitation. Once released into the atmosphere, these oxides and the compounds formed from them can travel great distances before returning to Earth in precipitation or as dry particulates, as much as 1,000 to 2,000 kilometers over three to five days. This long-range transport allows time for chemical reactions to convert pollutant gases into components of acid precipitation. Evidence suggests that the pH values in precipitation

have been dropping, becoming more acidic, for some years. Wet precipitation is not the only way pollutants find their way to the surface. Diffusion and settling enable acidic gases and particles to find their way to the ground even under dry conditions. It is now widely accepted that both wet and dry deposition can be traced to human activity.

Much evidence has been gathered documenting the damaging effects of acid precipitation. These effects include damage to wildlife in lakes and rivers, reduction of forest productivity, damage to agricultural crops, and deterioration of human-made materials. Acid precipitation, also suspected of promoting the release of heavy metals from soils and pipelines into drinking water supplies, has different effects on different ecological systems and is most damaging to aquatic ecosystems. Acidity in precipitation at a given time depends not only on the type and quantity of pollutants being produced but also on the prevailing and immediate atmospheric conditions. Stagnant air, resulting from upper-level inversions, tends to cause higher levels of acidity. Furthermore, prevailing and local atmospheric systems are associated with the spread of acid precipitation over broader areas. Higher exhaust stacks, while minimizing levels of air-borne pollutants locally, simply disperse the pollutants over larger areas, thus increasing their residence time in the atmosphere.

OZONE DEPLETION AND GLOBAL WARMING

It is now realized that the impact of air pollution is more far-reaching than the troposphere. Evidence indicates that pollutants making their way up to the stratosphere are causing the ozone layer to break down or dissipate. Even though ozone constitutes a very small portion of the atmosphere, only about one part per million, it absorbs almost all of the ultraviolet rays from the sun, preventing them from reaching Earth's surface. Research findings from satellite-based monitoring systems have shown that there has been a breakdown of the ozone shield over the Antarctic, where a hole has been identified in the ozone layer. More recent research and satellite-based observation has shown that the ozone layer also appears to be thinning over the Arctic.

While early laboratory studies showed that oxides of nitrogen could attack ozone, attention later focused on chlorofluorocarbons (CFCs) as being responsible for the decline in ozone. These

compounds were widely used as refrigerants in common household appliances and air conditioning systems, propellants in aerosol sprays, agents for producing foam, and cleansers for electronic products because they have low boiling points, facile compressibility, and very low chemical reactivity. Behaving much like inert gases, they do not degrade readily in the troposphere but eventually make their way into the stratosphere. Laboratory studies have shown that when the CFC molecules come in contact with ozone and ultraviolet light, they enter into a complex series of gas-phase reactions by which they are converted into more reactive gases, such as chlorine. Since these gases tend to linger in the atmosphere for many years, it is believed that even though several nations and the United States have banned the use of CFCs was discontinued, the ozone layer would continue to disintegrate for several years afterward. To further complicate the matter of CFCs and the recovery of the ozone layer, monitoring stations have identified a significant and steady increase in atmospheric levels of certain CFC compounds over the ten-year period from 2008 to 2018. Given the global ban on CFC production initiated by the Montreal Protocol, this indicates that someone somewhere has begun producing and continues to produce the material in bulk quantities in defiance of the global ban.

Further evidence suggests that CFCs not only destroy the ozone but also trap heat energy radiated from the ground and contribute to heating the atmosphere. The trapping of sensible heat energy in the atmosphere by gases is called the greenhouse effect. One of the most important gases contributing to the greenhouse effect, however, is not a chlorofluorocarbon but carbon dioxide. Carbon dioxide moves in a continuous cycle throughout the environment. It provides a link between the organic and inorganic components of the environment. Reacting with water and solar energy through photosynthesis in plants, it forms glucose that is subsequently passed through the food chain as a source of energy required by essentially all animal species.

Carbon dioxide is given off by plants and animals to the atmosphere during respiration. When plant and animal remains decay, carbon dioxide is passed back to the atmosphere and hydrosphere through the most natural processes of decomposition. When fossil fuels are burned, however, those natural processes