

Environmental Management & Pollution

SECONDARY ATMOSPHERIC POLLUTION

4.1 Secondary Atmospheric Pollutants

Secondary pollutants form when primary pollutants react in the atmosphere. Gases are present in the atmosphere at considerably lower concentrations than are typical for laboratory experiments or industrial processes, so molecules collide fairly infrequently.

4.2 Acid Deposition

Acid rain was first identified in the 19th century, when English pharmacist Robert Angus Smith measured high acidity levels in rain falling over industrial regions of England and much lower levels in less-polluted areas near the coast. However, this pattern did not receive sustained attention until biologists began to notice sharp declines in fish populations in lakes in Norway, the northeastern United States, and Canada in the 1950s and 1960s. In each case researchers found that acid precipitation was altering lake chemistry. These findings spurred research into the causes of acid rain.

Pure water has a pH value of 7 (neutral), but rainwater falling in the atmosphere always contains impurities. The atmosphere contains natural acids including CO₂ (a weak acid); nitric acid produced naturally from NO_x emitted by lightning, fires, and soils; and sulfuric acid produced by the oxidation of sulfur gases from volcanoes and the biosphere. It also contains natural bases, including ammonia (NH₃) emitted by the biosphere and calcium carbonate (CaCO₃) from suspended soil dust. CO₂ alone at natural levels (280 parts per million volume) would result in a rain pH of 5.7. Taken together, natural contaminants produce natural rain with pH values ranging from about 5 to 7 (recall that the pH scale is logarithmic, so one pH unit represents a factor of 10 difference in acid H⁺ concentration).

Acid rain refers to precipitation with pH values below 5, which generally happens only when large amounts of manmade pollution are added to the atmosphere. As acid deposition takes place throughout the eastern United States and is particularly severe in the industrial Midwest due to its concentration of coal-burning power plants. Tall power plant stacks built to protect local air quality inject SO₂ and NO_x

at high altitude where winds are strong, allowing acid rain to extend more than a thousand miles downwind and into Canada. The main components of acid rain worldwide are sulfuric acid and nitric acid. As discussed above in Section 3, these acids form when SO₂ and NO_x are oxidized in the atmosphere. Sulfuric and nitric acids dissolve in cloud-water and dissociate to release H⁺:

- HNO₃ (aq) → NO₃
- H₂SO₄(aq) → SO₄

Human activity also releases large amounts of ammonia to the atmosphere, mainly from agriculture, and this ammonia can act as a base in the atmosphere to neutralize acid rain by converting H⁺ to the ammonium ion (NH₄⁺). However, the benefit of this neutralization is illusory because NH₄⁺ releases its H⁺ once it is deposited and consumed by the biosphere. The relatively high pH of precipitation in the western United States is due in part to ammonia from agriculture and in part to suspended calcium carbonate (limestone) dust.

Acid rain has little effect on the environment in most of the world because it is quickly neutralized by naturally present bases after it falls. For example, the ocean contains a large supply of carbonate ions (CO₃²⁻), and many land regions have alkaline soils and rocks such as limestone. But in areas with little neutralizing capacity acid rain causes serious damage to plants, soils, streams, and lakes. In North America, the northeastern United States and eastern Canada are especially sensitive to acid rain because they have thin soils and granitic bedrock, which cannot neutralize acidity.

High acidity in lakes and rivers corrodes fishes' organic gill material and attacks their calcium carbonate skeletons. The acidity levels at which common freshwater organisms can live and reproduce successfully. Acid deposition also dissolves toxic metals such as aluminum in soil sediments, which can poison plants and animals that take the metals up. And acid rain increases leaching of nutrients from forest soils, which weakens plants and reduces their ability to weather other stresses such as droughts, air pollution, or bug infestation.

In addition to making ecosystems more acidic, deposition of nitrate and ammonia fertilizes ecosystems by providing nitrogen, which can be directly taken up by living organisms. Nitrogen pollution in rivers and streams is carried to the sea, where it contributes to algal blooms that deplete dissolved oxygen in coastal waters. As discussed in, "Water Resources," nutrient overloading has created dead zones in coastal regions around the globe, such as the Gulf of Mexico and the

Chesapeake Bay. The main sources of nutrient pollution are agricultural runoff and atmospheric deposition.

Acid rain levels have decreased and acid rain impacts have stabilized in the United States since SO₂ and NO_x pollution controls were tightened in 1990 (see Section 12, "Major Laws and Treaties," below). However, acid deposition is in large part a cumulative problem, as the acid-neutralizing capacity of soils is gradually eroded in response to acid input, and eventual exhaustion of this acid neutralizing capacity is a trigger for dramatic ecosystem impacts. Continued decrease in acid input is therefore critical.

4.3 Mercury Deposition

Mercury (Hg) is a toxic pollutant whose input to ecosystems has greatly increased over the past century due to anthropogenic emissions to the atmosphere and subsequent deposition. Mercury is ubiquitous in the environment and is unique among metals in that it is highly volatile. When materials containing mercury are burned, as in coal combustion or waste incineration, mercury is released to the atmosphere as a gas either in elemental form, Hg(0) or oxidized divalent form, Hg²⁺. The oxidized form is present as water-soluble compounds such as HgCl₂ that are readily deposited in the region of their emission. By contrast, Hg(0) is not water-soluble and must be oxidized to Hg²⁺ in order to be deposited. This oxidation takes place in the atmosphere on a time scale of one year, sufficiently long that mercury can be readily transported around the world by atmospheric circulation.

Mercury thus is a global pollution problem. Deposition of anthropogenically emitted mercury to land and ocean has considerably raised mercury levels in the biosphere. This accumulation is evident from sediment cores that provide historical records of mercury deposition for the past several centuries. Ice core samples from Antarctica, Greenland, and the western United States indicate that pre-industrial atmospheric mercury concentrations ranged from about 1 to 4 nanograms per liter, but that concentrations over the past 150 years have reached as high as 20 ng/L.

Once deposited, oxidized mercury can be converted back to the elemental form Hg(0) and re-emitted to the atmosphere. This repeated re-emission is called the "grasshopper effect," and can extend the environmental legacy of mercury emissions to several decades. The efficacy of re-emission increases with increasing temperature, which makes Hg(0) more volatile. As a result mercury tends to accumulate to particularly high levels in cold regions such as the Arctic where re-emission is slow.

Divalent mercury deposited to ecosystems can be converted by bacteria to organic methyl mercury, which is absorbed easily during digestion and accumulates in living tissues. It also enters fishes' bodies directly through their skin and gills. U.S. federal agencies and a number of states have issued warnings against consuming significant quantities of large predatory fish species such as shark and swordfish, especially for sensitive groups such as young children and women of childbearing age.

Mercury interferes with the brain and central nervous system. The expression "mad as a hatter" and the Mad Hatter character in Lewis Carroll's **Alice in Wonderland** are based on symptoms common among 19th-century English hat makers, who inhaled mercury vapors when they used a mercurous nitrate solution to cure furs. Many hatters developed severe muscle tremors, distorted speech, and hallucinations as a result sixty-eight people died and hundreds were made ill or born with neurological defects in Minamata, Japan in the 1950s and 1960s after a chemical company dumped mercury into Minamata Bay and families ate fish from the bay. Recently, doctors have reported symptoms including dizziness and blurred vision in healthy patients who ate significant quantities of high-mercury fish such as tuna.

Developed countries in North America and Europe are largely responsible for the global build-up of mercury in the environment over the past century. They have begun to decrease their emissions over the past two decades in response to the recognized environmental threat. However, emissions in Asia have been rapidly increasing and it is unclear how the global burden of mercury will evolve over the coming decades. Because mercury is transported on a global scale, its control requires a global perspective. In addition, the legacy of past emissions through re-emission and mercury accumulation in ecosystems must be recognized.

4.4 Controlling Air Pollution

Thanks to several decades of increasingly strict controls, emissions of most major air pollutants have declined in the U.S. and other industrialized countries since the 1970s. The aggregate decrease in U.S. emissions since 1970. This trend occurred even as economic activity and fuel consumption increased. The reductions came about because governments passed laws limiting allowable pollution levels and required the use of technologies to reduce emissions, such as scrubbers on power plant smokestacks and catalytic converters on vehicles.

This decrease in emissions has demonstrably reduced levels of the four principal primary pollutants:

- ✘ carbon monoxide,
- ✘ nitrogen dioxide,
- ✘ sulfur dioxide, and
- ✘ lead.

Air quality standards for these four pollutants were frequently exceeded in the U.S. twenty years ago but are hardly ever exceeded now. Progress in reducing the two principal secondary pollutants, ozone and particulate matter, has been much slower. This is largely due to nonlinear chemistry involved in the generation of these pollutants: reducing precursor emissions by a factor of two does not guarantee a corresponding factor of two decrease in the pollutant concentrations (the decrease is often much less, and there can even be an increase). In addition, advances in health-effects research have generated constant pressure for tougher air quality standards for ozone and fine aerosols.

In contrast to improvements in developed countries, air pollution has been worsening in many industrializing nations. Beijing, Mexico City, Cairo, Jakarta, and other megacities in developing countries have some of the dirtiest air in the world (for more on environmental conditions in megacities. This situation is caused by rapid population growth combined with rising energy demand, weak pollution control standards, dirty fuels, and inefficient technologies. Some governments have started to address this problem—for example, China is tightening motor vehicle emission standards—but much stronger actions will be required to reduce the serious public health impacts of air pollution worldwide.

4.5 Stratospheric Ozone

Earth's stratospheric ozone layer, which contains about 90 percent of the ozone in the atmosphere, makes the planet habitable by absorbing harmful solar ultraviolet (UV) radiation before it reaches the planet's surface. UV radiation damages cells and causes sunburn and premature skin aging in low doses. At higher levels, it can cause skin cancer and immune system suppression. Earth's stratospheric ozone layer absorbs 99 percent of incoming solar UV radiation.

Scientists have worked to understand the chemistry of the ozone layer since its discovery in the 1920s. In 1930 British geophysicist Sydney Chapman described a process in which strong UV photons photolyze oxygen molecules (O₂) into highly reactive oxygen atoms. These atoms rapidly combine with O₂ to form ozone (O₃).

This process is still recognized as the only significant source of ozone to the stratosphere. Research and controversy have focused on identifying stratospheric ozone sinks.

Ozone is produced by different processes in the stratosphere, where it is beneficial, and near the Earth's surface in the troposphere, where it is harmful. The mechanism for stratospheric ozone formation, photolysis of O₂, does not take place in the troposphere because the strong UV photons needed for this photolysis have been totally absorbed by O₂ and ozone in the stratosphere. In the troposphere, by contrast, abundance of VOCs promotes ozone formation by the mechanism described above. Ozone levels in the stratosphere are 10 to 100 times higher than what one observes at Earth's surface in the worst smog events. Fortunately we are not there to breathe it, though exposure of passengers in jet aircraft to stratospheric ozone has emerged recently as a matter of public health concern.

To explain observed stratospheric ozone concentrations, we need to balance ozone production and loss. Formation of ozone in the stratosphere is simple to understand, but the mechanisms for ozone loss are considerably more complicated. Ozone photolyzes to release O₂ and O, but this is not an actual sink since O₂ and O can just recombine to ozone. The main mechanism for ozone loss in the natural stratosphere is a catalytic cycle involving NO_x radicals, which speed up ozone loss by cycling between NO and NO₂ but are not consumed in the process.

The main source of NO_x in the troposphere is combustion; in contrast, the main source in the stratosphere is oxidation of nitrous oxide (N₂O), which is emitted ubiquitously by bacteria at the Earth's surface. Nitrous oxide is inert in the troposphere and can therefore be transported up to the stratosphere, where much stronger UV radiation enables its oxidation. Nitrous oxide emissions have increased over the past century due to agriculture, but the rise has been relatively modest (from 285 to 310 parts per million by volume) and of little consequence for the ozone layer.

In 1974 chemists Sherwood Roland and Mario Molina identified a major threat to the ozone layer: rising atmospheric concentrations of manmade industrial chemicals called chlorofluorocarbons (CFCs), which at the time were widely used as refrigerants, in aerosol sprays, and in manufacturing plastic foams. CFC molecules are inert in the troposphere, so they are transported to the stratosphere, where they photolyze and release chlorine (Cl) atoms. Chlorine atoms cause catalytic ozone loss by cycling with ClO.

Eventually chlorine radicals (Cl and ClO) are converted to the stable nonradical chlorine reservoirs of hydrogen chloride (HCl) and chlorine nitrate (ClNO₃). These reservoirs slowly "leak" by oxidation and photolysis to regenerate chlorine radicals. Chlorine is finally removed when it is transported to the troposphere and washed out through deposition. However, this transport process is slow. Concern over chlorine-catalyzed ozone loss through the mechanism led in the 1980s to the first measures to regulate production of CFCs.

In 1985 scientists from the British Arctic Survey reported that springtime stratospheric ozone levels over their station at Halley Bay had fallen sharply since the 1970s. Global satellite data soon showed that stratospheric ozone levels were decreasing over most of the southern polar latitudes. This pattern, widely referred to as the "ozone hole" (more accurately, ozone thinning), proved to be caused by high chlorine radical concentrations, as well as by bromine radicals (Br), which also trigger catalytic cycles with chlorine to consume ozone.

The source of the high chlorine radicals was found to be a fast reaction of the chlorine reservoirs HCl and ClNO₃ at the surface of icy particles formed at the very cold temperatures of the Antarctic wintertime stratosphere and called polar stratospheric clouds (PSCs). HCl and ClNO₃ react on PSC surfaces to produce molecular chlorine (Cl₂) and nitric acid. Cl₂ then rapidly photolyzes in spring to release chlorine atoms and trigger ozone loss.

Ozone depletion has worsened since 1985. Today springtime ozone levels over Antarctica are less than half of levels recorded in the 1960s, and the 2006 Antarctic ozone hole covered 29 million square kilometers, tying the largest value previously recorded in 200. In the 1990s ozone loss by the same mechanism was discovered in the Arctic springtime stratosphere, although Arctic ozone depletion is not as extensive as in Antarctica because temperatures are not as consistently cold.

Rowland and Molina's warnings about CFCs and ozone depletion, followed by the discovery of the ozone hole, spurred the negotiation of several international agreements to protect the ozone layer, leading eventually to a worldwide ban on CFC production in 1996. CFCs have lifetimes in the atmosphere of 50-100 years, so it will take that long for past damage to the ozone layer to be undone.

The Antarctic ozone hole is expected to gradually heal over the next several decades, but the effects of climate change pose major uncertainties. Greenhouse gases are well known to cool the stratosphere (although they warm the Earth's surface), and gradual decrease in stratospheric temperatures has been observed

over the past decades. Cooling of the polar stratosphere promotes the formation of PSCs and thus the release of chlorine radicals from chlorine reservoirs. The question now is whether the rate of decrease of stratospheric chlorine over the next decades will be sufficiently fast to stay ahead of the cooling caused by increasing greenhouse gases. This situation is being closely watched by atmospheric scientists both in Antarctica and the Arctic.

4.6 Air Pollution, Greenhouse Gases, and Climate Change

Air pollutants are major contributors to climate change. This connection is well known to scientists, although it has not yet permeated environmental policy. Figure 19 shows global climate forcing for the year 2000, relative to 1850, caused by different observed perturbations to the Earth system. Climate forcing from a given perturbation is defined as the mean resulting imbalance between energy input and energy output per unit time and unit area of Earth's surface (watts per square meter or W/m^2), with all else remaining constant, including temperature. A positive radiative forcing means a decrease in energy output and hence a warming. Negative radiative forcing, shown as blue bars, means a decrease in energy input and hence a cooling. A large number of perturbation agents have forced the climate since 1850. CO₂ is the single most important agent, but many other agents are also important and together exert greater influence than CO₂.

Among the major greenhouse gases are methane and tropospheric ozone, which are both of concern for air quality. Light absorption by black carbon aerosol particles also has a significant warming effect. Taken together these three agents produce more radiative forcing than CO₂. Reductions in these air pollutants thus would reap considerable benefit for climate change.

However, air pollutants can also have a cooling effect that compensates for greenhouse warming. This factor can be seen in Figure 19 from the negative radiative forcings due to non-light-absorbing sulfate and organic aerosols originating from fossil fuel combustion. Scattering by these aerosols is estimated by the Intergovernmental Panel on Climate Change (IPCC) to have a direct radiative forcing of $-1.3 W/m^2$, although this figure is highly uncertain. Indirect radiative forcing from increased cloud reflectivity due to anthropogenic aerosols is even more uncertain but could be as large as $-1 W/m^2$.

Scattering aerosols have thus masked a significant fraction of the warming imposed by increasing concentrations of greenhouse gases over the past two centuries. Aerosol and acid rain control policies, though undeniably urgent to

protect public health and ecosystems, will reduce this masking effect and expose us to more greenhouse warming. Influence also runs the other way. Global climate change has the potential to magnify air pollution problems by raising Earth's temperature (contributing to tropospheric ozone formation) and increasing the frequency of stagnation events. Climate change is also expected to cause more forest fires and dust storms, which can cause severe air quality problems.

The link between air pollution and climate change argues for developing environmental policies that will yield benefits in both areas. For example, researchers at Harvard University, Argonne National Laboratory, and the Environmental Protection Agency estimated in 2002 that reducing anthropogenic methane emissions by 50 percent would not only reduce greenhouse warming but also nearly halve the number of high-ozone events in the United States. Moreover, since methane contributes to background ozone levels worldwide, this approach would reduce ozone concentrations globally. In contrast, reducing NO_x emissions—the main U.S. strategy for combating ozone—produces more localized reductions to ozone.

Finally, let us draw the distinction between stratospheric ozone depletion and climate change, since these two problems are often confused in the popular press. The causes, processes, and impacts of these two global perturbations to the Earth system are completely different, but they have some links. On the one hand, colder stratospheric temperatures due to increasing greenhouse gases intensify polar ozone loss by promoting PSC formation. On the other hand, CFCs are major greenhouse gases, and stratospheric ozone depletion exerts a slight cooling effect on the Earth's surface.

4.7 Major Laws and Treaties

The first international treaty to protect the ozone layer was signed in 1987. The Montreal Protocol on Substances That Deplete the Ozone Layer has been amended several times since then in response to new scientific information, and it has been ratified by 190 countries. Under it industrialized countries phased out production of several classes of ozone-depleting substances by 1996, and developing countries are to follow suit by 2010. An international fund created under the protocol helps developing nations find substitutes for ozone-depleting substances. The World Bank estimates that reductions under the Montreal Protocol through 2003 have avoided up to 20 million cases of cancer, 130 million cases of eye cataracts, and severe damage to ecosystems from increased UV radiation reaching Earth's surface.

When nations began to negotiate agreements on reducing greenhouse gases to slow global climate change, many experts believed that the problem could be addressed through a framework similar to the Montreal Protocol—a treaty that set timetables for phasing out harmful emissions, with technical aid to help developing countries comply. But climate change has proved to be a considerably harder problem for negotiators, for several reasons.

The Clean Air Act (CAA) sets out a comprehensive set of national standards for controlling air pollutants that are considered harmful to public health and the environment in the United States. Under the CAA the Environmental Protection Agency is directed to establish National Ambient Air Quality Standards (NAAQS) limiting major air pollutants to levels that will protect public health, including the health of sensitive groups such as children, the elderly, and people with respiratory illnesses. NAAQS are set based on input from scientific advisory committees, and the act specifically directs EPA not to consider costs in setting NAAQS, although states can consider costs when they develop their plans for meeting the standards.

EPA has established NAAQS for six "criteria pollutants": SO₂, NO₂, lead, carbon monoxide, particulate matter less than 10 micrometers and less than 2.5 micrometers (PM-10 and PM-2.5), and ozone. States and counties that fail to achieve these standards are required to develop plans for bringing their air quality into compliance. The CAA also defines major pollution sources, based on their emission levels, and establishes rules governing when new emission sources can be built in polluted areas.

The CAA has been amended several times since its passage in 1970 to tighten standards and institute new controls that reflect advances in scientific understanding of air pollution. The law has achieved some notable successes: for example, it has reduced U.S. automobile emissions considerably from pre-1970 levels, through mechanisms such as phasing out use of leaded gasoline and requiring car manufacturers to install catalytic converters. These devices treat car exhaust in several stages to reduce NO_x and oxidize unburned hydrocarbons and carbon monoxide.

A set of CAA amendments passed in 1990 has produced significant cuts in SO₂ emissions through what was then a new approach to reducing air pollution: capping the total allowable amount of pollution emitted nationally and then allocating emission rights among major sources (mainly coal burning electric power plants and industrial facilities). Emitters that reduced pollution below their allowed levels could sell their extra pollution allowances to higher-emitting

sources. This approach let sources make reductions where they were cheapest, rather than requiring all emitters to install specific pieces of control equipment or to meet one standard at each location. Some companies cut emissions by installing controls, while others switched to low-sulfur coal or other cleaner fuels.

U.S. SO₂ emissions have fallen by roughly 50 percent since emissions trading was instituted, and the program is widely cited as an example of how this approach can work more effectively than technology mandates. However, some proposals for emissions trading are more controversial— specifically, whether it is a safe approach for cutting toxic pollutants such as mercury. Opponents argue that letting some large sources continue to emit such pollutants could create dangerous "hot spots" that would be hazardous to public health, and that the only safe way to control hazardous pollutants like mercury is to require specific reductions from each individual source.