

Environmental Management & Pollution

ATMOSPHERIC POLLUTION

3.1 Overview

Many forms of atmospheric pollution

affect human health and the environment at levels from local to global. These contaminants are emitted from diverse sources, and some of them react together to form new compounds in the air. Industrialized nations have made important progress toward controlling some pollutants in recent decades, but air quality is much worse in many developing countries, and global circulation patterns can transport some types of pollution rapidly around the world. In this unit, you will discover the basic chemistry of atmospheric pollution and learn which human activities have the greatest impacts on air quality.

3.2 Introduction of Atmospheric Pollution

The first week of December 1952 was unusually cold in London, so residents burned large quantities of coal in their fireplaces to keep warm. Early on December 5, moisture in the air began condensing into fog near the ground. The fog mixed with smoke from domestic fires and emissions from factories and diesel-powered buses. Normally the fog would have risen higher in the atmosphere and dispersed, but cold air kept it trapped near the ground. Over the next four days, the smog became so thick and dense that many parts of London were brought to a standstill.

Public officials did not realize that the Great Smog was the most deadly air pollution event on record until mortality figures were published several weeks afterward. Some 4,000 people died in London between December 5-9 of illnesses linked to respiratory problems such as bronchitis and pneumonia, and the smog's effects caused another 8,000 deaths over the next several months. Samples showed that victims' lungs contained high levels of very fine particles, including carbon material and heavy metals such as lead, zinc, tin, and iron.

Air pollution was not news in 1952—London's air had been famously smoky for centuries—but the Great Smog showed that it could be deadly. The event spurred some of the first governmental actions to reduce emissions from fuel combustion, industrial operations, and other manmade sources. Over the past half-century, scientists have learned much more about the causes and impacts of atmospheric pollution. Many nations have greatly reduced their emissions, but the problem is

far from solved. In addition to threatening human health, air pollutants damage ecosystems, weaken Earth's stratospheric ozone shield, and contribute to global climate change.

Understanding of pollutants is still evolving, but we have learned enough to develop emission control policies that can limit their harmful effects. Some major pollutants contribute to both air pollution and global climate change, so reducing these emissions has the potential to deliver significant benefits. To integrate air pollution and climate change strategies effectively, policy makers need extensive information about key pollutants and their interactions. This unit describes the most important types of pollutants affecting air quality and the environment. It also summarizes some widely used technical and policy options for controlling atmospheric pollution, and briefly describes important laws and treaties that regulate air emissions.

3.3 Chemicals in Motion

The science of air pollution centers on measuring, tracking, and predicting concentrations of key chemicals in the atmosphere. Four types of processes affect air pollution levels:

- 1) **Emissions.** Chemicals are emitted to the atmosphere by a range of sources. Anthropogenic emissions come from human activities, such as burning fossil fuel. Biogenic emissions are produced by natural functions of biological organisms, such as microbial breakdown of organic materials. Emissions can also come from nonliving natural sources, most notably volcanic eruptions and desert dust.
- 2) **Chemistry.** Many types of chemical reactions in the atmosphere create, modify, and destroy chemical pollutants. These processes are discussed in the following sections.
- 3) **Transport.** Winds can carry pollutants far from their sources, so that emissions in one region cause environmental impacts far away. Long-range transport complicates efforts to control air pollution because it can be hard to distinguish effects caused by local versus distant sources and to determine who should bear the costs of reducing emissions.
- 4) **Deposition.** Materials in the atmosphere return to Earth, either because they are directly absorbed or taken up in a chemical reaction (such as

photosynthesis) or because they are scavenged from the atmosphere and carried to Earth by rain, snow, or fog.

Air pollution trends are strongly affected by atmospheric conditions such as temperature, pressure, and humidity, and by global circulation patterns. For example, winds carry some pollutants far from their sources across national boundaries and even across the oceans. Transport is fastest along east-west routes: longitudinal winds can move air around the globe in a few weeks, compared to months or longer for air exchanges from north to south (for more details see Unit 2, "Atmosphere").

Local weather patterns also interact with and affect air pollution. Rain and snow carry atmospheric pollutants to Earth. Temperature inversions, like the conditions that caused London's Great Smog in 1952, occur when air near the Earth's surface is colder than air aloft. Cold air is heavier than warm air, so temperature inversions limit vertical mixing and trap pollutants near Earth's surface. Such conditions are often found at night and during the winter months. Stagnation events characterized by weak winds are frequent during summer and can lead to accumulation of pollutants over several days.

To see the close connections between weather, climate, and air pollution, consider Los Angeles, whose severe air quality problems stem partly from its physical setting and weather patterns. Los Angeles sits in a bowl, ringed by mountains to the north and east that trap pollutants in the urban basin. In warm weather, cool sea breezes are drawn onshore at ground level, creating temperature inversions that prevent pollutants from rising and dissipating. The region's diverse manufacturing and industrial emitters and millions of cars and trucks produce copious primary air pollutants that mix in its air space to form photochemical smog.

Scientists can measure air pollutants directly when they are emitted—for example, by placing instruments on factory smokestacks—or as concentrations in the ambient outdoor air. To track ambient concentrations, researchers create networks of air-monitoring stations, which can be ground based or mounted on vehicles, balloons, airplanes, or satellites.

In the laboratory, scientists use tools including laser spectrometers and electron microscopes to identify specific pollutants. They measure chemical reaction rates in clear plastic bags ("smog chambers") that replicate the smog environment under controlled conditions, and observe emission of pollutants from combustion and other sources. Knowledge of pollutant emissions, chemistry, and transport can be

incorporated into computer simulations ("air quality models") to predict how specific actions, such as requiring new vehicle emission controls or cleaner-burning fuels, will benefit ambient air quality. However, air pollutants pass through many complex reactions in the atmosphere and their residence times vary widely, so it is not always straightforward to estimate how emission reductions from specific sources will impact air quality over time.

3.4 Primary Air Pollutants

Primary air pollutants are emitted directly into the air from sources. They can have effects both directly and as precursors of secondary air pollutants (chemicals formed through reactions in the atmosphere), which are discussed in the following section.

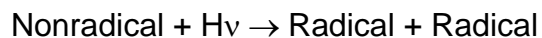
- ☠ Sulfur dioxide (SO₂) is a gas formed when sulfur is exposed to oxygen at high temperatures during fossil fuel combustion, oil refining, or metal smelting. SO₂ is toxic at high concentrations, but its principal air pollution effects are associated with the formation of acid rain and aerosols. SO₂ dissolves in cloud droplets and oxidizes to form sulfuric acid (H₂SO₄), which can fall to Earth as acid rain or snow or form sulfate aerosol particles in the atmosphere. Associated impacts are discussed below.
- ☠ Nitrogen oxides (NO and NO₂, referred together as NO_x) are highly reactive gases formed when oxygen and nitrogen react at high temperatures during combustion or lightning strikes. Nitrogen present in fuel can also be emitted as NO_x during combustion. Emissions are dominated by fossil fuel combustion at northern mid-latitudes and by biomass burning in the tropics. The distribution of NO_x emissions to the atmosphere in 2006 as determined by satellite measurements of atmospheric NO₂ concentrations.
 - In the atmosphere NO_x reacts with volatile organic compounds (VOCs) and carbon monoxide to produce ground-level ozone through a complicated chain reaction mechanism. It is eventually oxidized to nitric acid (HNO₃). Like sulfuric acid, nitric acid contributes to acid deposition and to aerosol formation.
- ☠ Carbon monoxide (CO) is an odorless, colorless gas formed by incomplete combustion of carbon in fuel. The main source is motor vehicle exhaust, along with industrial processes and biomass burning. Carbon monoxide binds to hemoglobin in red blood cells, reducing their ability to transport and

release oxygen throughout the body. Low exposures can aggravate cardiac ailments, while high exposures cause central nervous system impairment or death. It also plays a role in the generation of ground-level ozone, discussed below in.

- ☠ Volatile organic compounds (VOCs), including hydrocarbons (C_xH_y) but also other organic chemicals are emitted from a very wide range of sources, including fossil fuel combustion, industrial activities, and natural emissions from vegetation and fires. Some anthropogenic VOCs such as benzene are known carcinogens. VOCs are also of interest as chemical precursors of ground-level ozone and aerosols, as discussed.
 - The importance of VOCs as precursors depends on their chemical structure and atmospheric lifetime, which can vary considerably from compound to compound. Large VOCs oxidize in the atmosphere to produce nonvolatile chemicals that condense to form aerosols. Short-lived VOCs interact with NO_x to produce high ground-level ozone in polluted environments. Methane (CH₄), the simplest and most long-lived VOC, is of importance both as a green-house gas and as a source of background tropospheric ozone. Major anthropogenic sources of methane include natural gas production and use, coal mining, livestock, and rice paddies.

3.5 Radical Formations

As a result, most atmospheric reactions that occur at significant rates involve at least one radical—a molecule with an odd number of electrons and hence an unpaired electron in its outer shell. The unpaired electron makes the radical unstable and highly reactive with other molecules. Radicals are formed when stable molecules are broken apart, a process that requires large amounts of energy. This can take place in combustion chambers due to high temperatures, and in the atmosphere by photolysis:

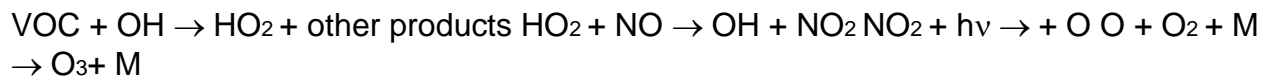


Radical formation initiates reaction chains that continue until radicals combine with other radicals to produce nonradicals (atoms with an even number of electrons). Radical-assisted chain reactions in the atmosphere are often referred to as photochemical mechanisms because sunlight plays a key role in launching them.

(NMVOCs). Some of these reactions eventually regenerate OH in continuous cycles, while others deplete it.

Since OH has a short atmospheric lifetime, its concentration can vary widely. Some anthropogenic emissions, such as carbon monoxide and VOCs, deplete OH, while others such as NO_x boost OH levels. Measuring atmospheric OH is difficult because its concentration is so low. Long-term trends in OH concentrations are uncertain, although the prevailing view is that trends over the past decades have been weak because of compensating influences from carbon monoxide and VOCs on the one hand and NO_x on the other hand. Since OH affects the rates at which some pollutants are formed and others are destroyed, changes in OH levels over the long term would have serious implications for air quality.

Ground-level ozone (O₃) is a pernicious secondary air pollutant, toxic to both humans and vegetation. It is formed in surface air (and more generally in the troposphere) by oxidation of VOCs and carbon monoxide in the presence of NO_x. The mechanism is complicated, involving hundreds of chemically interactive species to describe the VOC degradation pathways. A simple schematic is:



An important aspect of this mechanism is that NO_x and OH act as catalysts—that is, they speed up the rate of ozone generation without being consumed themselves. Instead they cycle rapidly between NO and NO₂, and between OH and HO₂.

One of the most important radicals in atmospheric chemistry is the hydroxyl radical (OH), sometimes referred to as the atmospheric cleanser. OH is produced mainly through photolysis reactions that break apart tropospheric ozone, and is very short-lived. It is consumed within about one second by oxidizing a number of trace gases like carbon monoxide, methane, and non-methane VOCs.

This formation mechanism for ozone at ground level is totally different from that for ozone formation in the stratosphere, where 90 percent of total atmospheric ozone resides and plays a critical role in protecting life on Earth by providing a UV shield. In the stratosphere ozone is produced from photolysis of oxygen ($\text{O}_2 + h\nu \rightarrow \text{O} + \text{O}$, followed by $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$). This process does not take place in the troposphere because the strong (< 240 nm) UV photons needed to dissociate molecular oxygen are depleted by the ozone overhead.

2.6 Aerosols

In addition to gases, the atmosphere contains solid and liquid particles that are suspended in the air. These particles are referred to as aerosols or particulate matter (PM). Aerosols in the atmosphere typically measure between 0.01 and 10 micrometers in diameter, a fraction of the width of a human hair. Most aerosols are found in the lower troposphere, where they have a residence time of a few days. They are removed when rain or snow carries them out of the atmosphere or when larger particles settle out of suspension due to gravity.

Large aerosol particles (usually 1 to 10 micrometers in diameter) are generated when winds blow sea salt, dust, and other debris into the atmosphere. Fine aerosol particles with diameters less than 1 micrometer are mainly produced when precursor gases condense in the atmosphere. Major components of fine aerosols are sulfate, nitrate, organic carbon, and elemental carbon. Sulfate, nitrate, and organic carbon particles are produced by atmospheric oxidation of SO₂, NO_x, and VOCs as discussed above in Section 3.

Elemental carbon particles are emitted by combustion, which is also a major source of organic carbon particles. Light-absorbing carbon particles emitted by combustion are called black carbon or soot; they are important agents for climate change and are also suspected to be particularly hazardous for human health.

High concentrations of aerosols are a major cause of cardiovascular disease and are also suspected to cause cancer. Fine particles are especially serious threats because they are small enough to be absorbed deeply into the lungs, and sometimes even into the bloodstream. Scientific research into the negative health effects of fine particulate air pollution spurred the U.S. Environmental Protection Agency to set limits in 1987 for exposure to particles with a diameter of 10 micrometers or less, and in 1997 for particles with a diameter of 2.5 micrometers or less.

Aerosols also have important radiative effects in the atmosphere. Particles are said to scatter light when they alter the direction of radiation beams without absorbing radiation. This is the principal mechanism limiting visibility in the atmosphere, as it prevents us from distinguishing an object from the background. Air molecules are inefficient scatterers because their sizes are orders of magnitude smaller than the wavelengths of visible radiation (0.4 to 0.7 micrometers). Aerosol particles, by contrast, are efficient scatterers. When relative humidity is high, aerosols absorb water, which causes them to swell and increases their cross-sectional area for scattering, creating haze. Without aerosol pollution our visual range would typically be about 200 miles, but haze can reduce visibility significantly.

Aerosols have a cooling effect on Earth's climate when they scatter solar radiation because some of the scattered light is reflected back into space. Earth's Changing Climate, such as a major volcanic eruptions that inject large quantities of aerosols into the stratosphere, such as that of Mt. Pinatubo in 1991, can noticeably reduce average global surface temperatures for some time afterward.

In contrast, some aerosol particles such as soot absorb radiation and have a warming effect. This means that estimating the net direct contribution to global climate change from aerosols requires detailed inventories of the types of aerosols in the atmosphere and their distribution around the globe.

Aerosol particles also influence Earth's climate indirectly: they serve as condensation nuclei for cloud droplets, increasing the amount of radiation reflected back into space by clouds and modifying the ability of clouds to precipitate. The latter is the idea behind "cloud seeding" in desert areas, where specific kinds of mineral aerosol particles that promote ice formation are injected into a cloud to make it precipitate.

Aerosol concentrations vary widely around the Earth. Measurements are tricky because the particles are difficult to collect without modifying their composition. Combined optical and mass spectrometry techniques that analyze the composition of single particles directly in an air flow, rather than recovering a bulk composition from filters, have improved scientists' ability to detect and characterize aerosols.

One important research challenge is learning more about organic aerosols, which typically account for a third to half of total aerosol mass. These include many types of carbon compounds with diverse properties and environmental impacts. Organic aerosols are emitted to the atmosphere directly by inefficient combustion. Automobiles, wood stoves, agricultural fires, and wildfires are major sources in the United States.

Atmospheric oxidation of VOCs, both anthropogenic and biogenic, is another major source in summer. The relative importance of these different sources is still highly uncertain, which presently limits our ability to assess anthropogenic influence and develop strategies for reducing concentrations.

3.7 Smog

Smog is often used as a generic term for any kind of air pollution that reduces visibility, especially in urban areas. However, it is useful to distinguish two broad

types: industrial smog and photochemical smog. Events like the London smog of 1952 are often referred to as industrial smog because SO₂ emissions from burning coal play a key role.

Typically, industrial smog—also called gray or black smog—develops under cold and humid conditions. Cold temperatures are often associated with inversions that trap the pollution near the surface (see "Chemicals in Motion," above). High humidity allows for rapid oxidation of SO₂ to form sulfuric acid and sulfate particles. Events similar to the 1952 London smog occurred in the industrial towns of Liege, Belgium, in 1930, killing more than 60 people, and Donora, Pennsylvania, in 1948, killing 20. Today coal combustion is a major contributor to urban air pollution in China, especially from emissions of SO₂ and aerosols.

Air pollution regulations in developed countries have reduced industrial smog events, but photochemical smog remains a persistent problem, largely driven by vehicle emissions. Photochemical smog forms when NO_x and VOCs react in the presence of solar radiation to form ozone. The solar radiation also promotes formation of secondary aerosol particles from oxidation of NO_x, VOCs, and SO₂. Photochemical smog typically develops in summer (when solar radiation is strongest) in stagnant conditions promoted by temperature inversions and weak winds.

Photochemical smog is a ubiquitous urban problem in the developed world and often blankets large populated regions such as the eastern United States and Western Europe for extended periods in summer.

Ozone and aerosols are the two main health hazards of photochemical smog. Ozone is invisible, but aerosol particles scatter sunlight as discussed above in Section 5, and are responsible for the whitish haze associated with smog. Because ozone is created in the atmosphere, concentrations are often higher downwind of urban areas than in the urban areas themselves. Some counties in the United States that currently fail to comply with the national standard for ozone levels over an 8-hour period (nonattainment areas). These cover much of California and the eastern United States on a regional scale.