# Nitrogen Oxides

Nitrogen oxides (NO<sub>x</sub>) in the ambient air consist primarily of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). These two forms of gaseous nitrogen oxides are significant pollutants of the lower atmosphere. Another form, nitrous oxide (N2O), is a greenhouse gas. At the point of discharge from man-made sources, nitric oxide, a colorless, tasteless gas, is the predominant form of nitrogen oxide. Nitric oxide is readily converted to the much more harmful nitrogen dioxide by chemical reaction with ozone present in the atmosphere. Nitrogen dioxide is a yellowish-orange to reddish-brown gas with a pungent, irritating odor, and it is a strong oxidant. A portion of nitrogen dioxide in the atmosphere is converted to nitric acid (HNO<sub>3</sub>) and ammonium salts. Nitrate aerosol (acid aerosol) is removed from the atmosphere through wet or dry deposition processes similar to those that remove sulfate aerosol.

## **Major Sources**

Only about 10% of all  $NO_x$  emissions come from anthropogenic sources (Godish 1991). The rest is produced naturally by anaerobic biological processes in soil and water, by lightning and volcanic activity, and by photochemical destruction of nitrogen compounds in the upper atmosphere. About 50% of emissions from anthropogenic sources comes from fossil-fuel-fired heat and electricity generating plants and slightly less from motor vehicles. Other sources include industrial boilers, incinerators, the manufacture of nitric acid and other nitrogenous chemicals, electric arc welding processes, the use of explosives in mining, and farm silos.

Worldwide annual emissions of anthropogenic nitrogen oxides are estimated at approximately 50 million metric tons (World Resources Institute 1994). The United States generates about 20 million metric tons of nitrogen oxides per year, about 40% of which is emitted from mobile sources. Of the 11 million to 12 million metric tons of nitrogen oxides that originate from stationary sources, about 30% is the result of fuel combustion in large industrial furnaces and 70% is from electric utility furnaces (Cooper and Alley 1986).

## Occurrence in Air and Routes of Exposure

Annual mean concentrations of nitrogen dioxide in urban areas throughout the world are in the range of 20–90 micrograms per cubic meter (µg/ m³). Maximum half-hour values and maximum 24hour values of nitrogen dioxide can approach 850 μg/m³ and 400 μg/m³, respectively. Hourly averages near very busy roads often exceed 1,000 µg/ m3. Urban outdoor levels of nitrogen dioxide vary according to time of day, season, and meteorological conditions. Typically, urban concentrations peak during the morning and afternoon rush hours. Levels are also higher in winter in cold regions of the world than in other seasons because of the increased use of heating fuels. Finally, since the conversion of nitrogen dioxide from nitric oxide depends on solar intensity, concentrations are often greater on warm, sunny days. Nitrogen oxides decay rapidly as polluted air moves away from the source. Concentrations of nitrogen oxides in rural areas without major sources are typically close to background levels. However, nitrogen oxides can travel long distances in the upper atmosphere, contributing to elevated ozone levels and acidic depositions far from sources of emissions.

Concentrations of nitrogen dioxide in homes may considerably exceed outdoor levels and may therefore be more important for human health. Large sources of indoor nitrogen dioxide include cigarette smoke, gas-fired appliances, and space heaters. Nitrogen dioxide concentrations in kitchens with unvented gas appliances can exceed 200  $\mu g/m^3$  over a period of several days. Maximum 1-hour concentrations during cooking may reach 500–1,900  $\mu g/m^3$ , and 1,000–2,000  $\mu g/m^3$  where a gas-fired water heater is also in use. Smoke from one cigarette may contain 150,000–225,000  $\mu g/m^3$  of nitric oxide and somewhat less nitrogen dioxide.

# **Health and Environmental Impacts**

#### Health

Epidemiologic studies have rarely detected effects on children or adults from exposure to outdoor nitrogen dioxide. One study of nurses in Los Angeles found an association between exposure to nitrogen dioxide and increased phlegm production (Schwartz and Zegler 1990). Studies have indicated that the use of gas appliances for cooking may have a very small effect on the human respiratory system, especially for small children, but that the effect (if it exists) disappears as the children grow older (WHO 1987).

Available data from animal toxicological experiments rarely indicate effects of acute exposure to nitrogen dioxide concentrations of less than 1,880 μg/m³ (WHO 1987). Asthmatics are likely to be the group most sensitive to exposure to nitrogen oxides. Two laboratories have reported reversible effects on pulmonary function of asthmatics exercising intermittently after 30 minutes of exposure to nitrogen dioxide concentrations as low as 560 µg/m³ (WHO 1987). However, the health impact of the change in pulmonary function is unclear; the change of about 10% is within the range of physiological variation and is not necessarily adverse. At levels above 3,760 µg/m³, normal subjects have demonstrated substantial changes in pulmonary function (WHO 1987).

Studies with animals have found that several weeks to months of exposure to nitrogen dioxide concentrations less than 1,880  $\mu g/m^3$  causes both reversible and irreversible lung effects and biochemical changes. Animals exposed to nitrogen dioxide levels as low as 940  $\mu g/m^3$  for six months may experience destruction of cilia, alveolar tis-

sue disruption, obstruction of the respiratory bronchioles, and increased susceptibility to bacterial infection of the lungs (WHO 1987). Rats and rabbits exposed to higher levels experience more severe tissue damage, resembling emphysema.

The available data suggest that the physiological effects of nitrogen dioxide on humans and animals are due more to peak concentrations than to duration or to total dose.

#### Materials

Nitrogen dioxide in reaction to textile dyes can cause fading or yellowing of fabrics. Exposure to nitrogen dioxide can also weaken fabrics or reduce their affinity for certain dyes. Industry has devoted considerable resources to developing textiles and dyes resistant to nitrogen oxide exposure (Canada 1987).

### Effects on Ecosystems

Nitrogen oxides are precursors of both acid precipitation and ozone, each of which is blamed for injury to plants. While nitric acid is responsible for only a smaller part of hydrogen ion ( $H^+$ ) concentration in wet and dry acid depositions, the contribution of nitrogen oxide emissions to acid deposition could be more significant. It is nitrogen oxide that absorbs sunlight, initiating the photochemical processes that produce nitric acid. Approximately 90–95% of the nitrogen oxides emitted from power plants is nitric oxide; this slowly converts to nitrogen dioxide in the presence of ozone.

The extent and severity of the damage attributable to acid depositions is difficult to estimate, since impacts vary according to soil type, plant species, atmospheric conditions, insect populations, and other factors that are not well understood. Nitrates in precipitation may actually increase forest growth in areas with nitrogen-deficient soils. However, the fertilizing effect of nitrates (and sulfates) may be counterbalanced by the leaching of potassium, magnesium, calcium, and other nutrients from forest soils. There is little evidence that agricultural crops are being injured by exposures to nitrates in precipitation. The amount of nitrates in rainwater is almost always

well below the levels applied as fertilizer (NAPAP 1990).

The most evident damage from acid depositions is to freshwater lake and stream ecosystems. Acid depositions can lower the pH of the water, with potentially serious consequences for fish, other animal, and plant life. Lakes in areas with soils containing only small amounts of calcium or magnesium carbonates that could help neutralize acidified rain are especially at risk. Few fish species can survive the sudden shifts in pH (and the effects of soluble substances) resulting from atmospheric depositions and runoff of contaminated waters; affected lakes may become completely devoid of fish life. Acidification also decreases the species variety and abundance of other animal and plant life. "Acid pulses" have been associated with the fish kills observed in sensitive watersheds during the spring meltdown of the snowpack. The atmospheric deposition of nitrogen oxides is a substantial source of nutrients that damage estuaries by causing algal blooms and anoxic conditions.

Emissions of nitrogen oxides are a precursor of ground-level ozone (O<sub>3</sub>), which is potentially a more serious problem. Plant scientists blame tropospheric ozone for 90% of the injury to vegetation in North America. Ozone can travel long distances from the source and can contribute to elevated ozone concentrations even in rural areas. Since the meteorological and climatic conditions that favor the production of ozone—abundant sunshine—are also good for agriculture, ozone has the potential to cause large economic losses from reductions in crop yields.

Nitrogen dioxide affects visibility by absorbing short-wavelength blue light. Since only the longer

wavelengths of light are visible to the eye, nitrogen dioxide appears yellowish to reddish-brown in color. Nitrogen oxides can also combine with photochemical oxidants to form smog.

## **Ambient Standards and Guidelines**

The main goal of almost all the major national and international air quality standards and guidelines produced over the last two decades has been to protect human health. Some countries have also produced guidelines and standards for nitrogen oxides to protect vegetation and sensitive ecosystems, such as wetlands. Table 1 presents EU, USEPA, and WHO reference standards and guidelines for ambient levels of nitrogen dioxide.

#### **Conclusions**

The evidence suggests that exposure to short-term peak concentrations of nitrogen dioxide may damage health, especially of sensitive individuals such as asthmatics. For many individuals, the most significant sources of repetitive exposure to peak levels of nitrogen oxides come from residing in homes with gas cooking or heating appliances or from cigarette smoking. Long-term exposures to high levels of nitrogen dioxide (well above the highest ambient levels reported in urban areas in the United States) has been shown to lead to development of chronic lung injury and disease in animals. However, there is still considerable uncertainty regarding chronic health effects for humans from exposure to ambient nitrogen oxides (NAPAP 1991).

Table 1. Reference Standards and Guidelines for Ambient Levels of Nitrogen Dioxide (micrograms per cubic meter)

Standard or guideline	Annual average	24-hour average	1-hour average
EU limit values (1985)	200a		
USEPA standards (1992)	100 <sup>b</sup>		
WHO guidelines (1977)			190–320∘
WHO guidelines for Europe (1987)		150	400

a. 98th percentile calculated from the mean values per hour or per period of less than an hour taken throughout the year.

b. Arithmetic mean.

c. Not to be exceeded more than once a month. Only a short-term exposure limit has been suggested. *Sources:* European Community 1985 (EU); United States 1992, 40 CFR, Part 60; WHO 1977, 1987.

#### Recommendations

In the long term, countries should seek to ensure that ambient exposure to nitrogen dioxide does not exceed the WHO recommended guidelines. In the interim, countries should set ambient standards for nitrogen dioxide that take into account the benefits to human health and to sensitive ecosystems of reducing exposure to nitrogen dioxide; the concentration levels achievable by pollution prevention and control measures; and the costs involved in meeting the standards. In adopting new ambient air quality standards, countries should set appropriate phase-in periods during which districts or municipalities that do not meet the new standards are expected and will be assisted to attain these standards. Where there are large differences between the costs and benefits of meeting air quality standards, it may be appropriate to establish area-specific ambient standards case by case.

Prior to carrying out an environmental assessment (EA), a trigger value for the annual average concentrations of nitrogen oxides should be agreed on by the country and the World Bank Group. Countries may wish to adopt EU, USEPA, or WHO guidelines or standards as their trigger values. The trigger value should be equal to or lower than the country's ambient standard. The trigger value is not an ambient air quality standard but simply a threshold. If, as a result of the project, the trigger value is predicted to be exceeded in the area affected by the project, the EA should seek mitigation alternatives on a regional or sectoral basis. The World Bank Group will classify airsheds as moderately degraded if concentration levels are above 100 µg/m³ annual average or if the 98th percentile of 24-hour mean values over a period of one year is estimated to exceed 150 µg/m³ of nitrogen oxides. Airsheds will be classified as having poor air quality with respect to nitrogen dioxide if the 95th percentile of 24-hour mean values of nitrogen dioxide for the airshed over a period of one year is estimated to exceed  $150 \, \mu g/m^3$ .

Good practice in airshed management should encompass the establishment of an emergency response plan during industrial plant operation. It is recommended that this plan be put into effect when levels of air pollution exceed one or more of the emergency trigger values (determined for short-term concentrations of sulfur dioxide, nitrogen oxides, particulates, and ozone). The recommended emergency trigger value for nitrogen oxides is 150  $\mu g/m^3$  for the 24-hour average concentrations.

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