Sustainability Profile: NO_x and SO_x

Carbon dioxide, CO_2, is a well-studied molecule associated with climate change, but it is not the only non-metal oxide of environmental importance. NO_x and SO_x are abbreviated formulas referring to a variety of molecules formed through natural and industrial processes. The subscript "x" in NO_x and SO_x refers to the number of oxygens bound to the central atom in each case. These molecules play an important role in smog and atmospheric pollution leading to acid rain and health-related air-quality issues.

Under normal atmospheric conditions, nitrogen and oxygen gases do not react with one another because more energy is required than is available. As the combustion engines in cars heat up and release CO_2 from hydrocarbon combustion into the atmosphere, the endothermic reaction below proceeds.

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H = 180.5$ kJ

According to the EPA, over 55% of NO_x total emissions in the US are from the transportation sector, but there are also natural sources of NO_x gases. Lightning is a natural source of NO_x gases since it supplies temperatures high enough to power the endothermic reactions needed to break apart the relatively inert N_2 molecules in air. In large cities, such as Denver and other high-traffic communities along the Front Range, this is particularly important because of the chain of reactions that follow the initial formation of NO. NO can further react with O_2 to form NO_2.

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

The reddish-brown color of NO_2 is a significant contributor to the brown haze associated with the air in high-traffic areas. The production of NO_2 is quite rapid once NO is available in sufficient concentrations. When sunlight hits NO_2 (such as during daylight hours in commuter traffic) it breaks apart and releases NO again as well as reactive oxygen radicals. The interconnectedness of these processes and the dependence upon sunlight in some cases mean that the concentrations of gases are in constant flux, but that the rate of each process depends upon the concentrations of the reactant gases.

$NO_2(g) \xrightarrow{\lambda<424\text{nm}} NO(g) + O(g)$ (reaction 1, with the rate constant k_1, depends on light)

This reactive oxygen is what can produce both ozone (O_3) and hydroxyl radicals with other common gases in the atmosphere. Ozone is formed in the upper atmosphere about 10 to 50 km above the earth's surface, where it absorbs harmful ultraviolet radiation before it reaches ground level. When inhaled, ozone acts as a dangerous irritant, so its production in the lower atmosphere is not desirable.

$O(g) + O_2(g) \rightarrow O_3(g)$ (reaction 2, with the rate constant k_2)

$O(g) + H_2O(g) \rightarrow 2OH(g)$

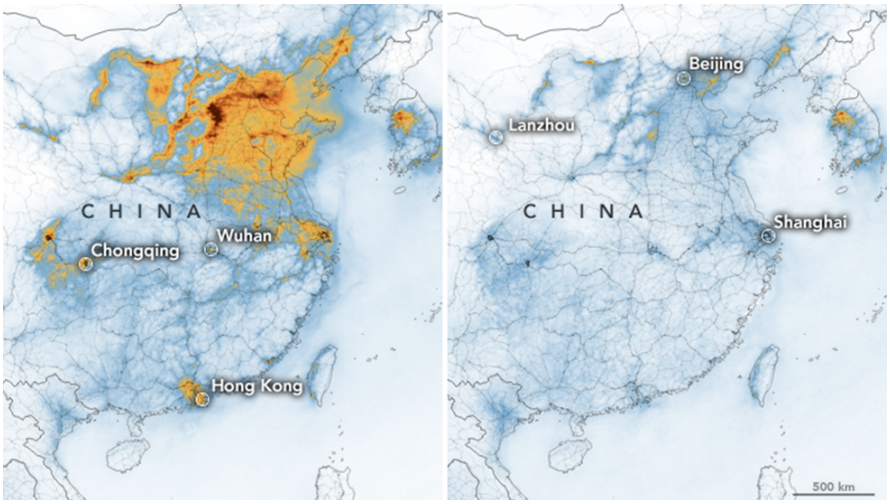
Volatile organic compounds (VOCs) are organic molecules that easily go into the gas phase. Industrial activities and transportation are common sources of atmospheric hydrocarbons which react with NO_x to form ozone and peroxides such as peroxyacetyl nitrate (PAN) – an unstable molecule that irritates the lungs and eyes. Ozone, VOCs and OH radicals go on to produce even more of the environmental irritants that comprise photochemical smog, or react to produce more NO_2.

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ (reaction 3, with the rate constant k_3)

Fundamentally, the concentrations of these gases are related through the Leighton relationship (shown below) such that the concentrations of NO_x gases determines the concentration of ozone in the air.

$[NO_2]/[NO] = k_3[O_3]/k_1$

Because these reactions are dependent upon the heat associated with internal combustion engines and in some cases with the absorption of sunlight, the concentrations of the different components of smog in a high traffic area fluctuate over the course of a day, and with the time of year (since sunlight time and intensity vary with the seasons). Removing traffic and industrial sources of internal combustion engine use significantly and quickly removes NO_x from the atmosphere. NASA and European Space Agency pollution monitoring satellites detected significant decreases in nitrogen dioxide over China that researchers think was connected to the economic slowdown caused by the outbreak of coronavirus in 2020. The maps below show NO_2 values across China from January 1-20, 2020, (before the quarantine) and February 10-25 (during the quarantine). (NASA Earth Observatory images by Joshua Stevens, using modified Copernicus Sentinel 5P data processed by the European Space Agency).



The use of catalytic converters rapidly reacts NO_x gases as well as CO and unburned hydrocarbons to less-damaging products such as CO_2, water and N_2.

Although the term NO_x generally refers to varying the number of oxygens around a single N, the term also applies to N_2O, nitrous oxide. Nitrous oxide is used as an anesthetic and as a propellant for whipped cream and other foaming sprays. Although it is not considered to have a role in air pollution, it is a potent greenhouse gas, and it may play a role in depletion of the ozone layer.

The term SO_x generally refers to SO_2, sulfur dioxide, and SO_3, sulfur trioxide. These nonmetal oxides are formed from burning sulfur-containing substances, and they are associated with both volcanic gases and industrial plants that burn fuels that contain sulfur (such as coal). Roasting metal sulfides from rocks (such as in smelting to eventually isolate the metal) also releases SO_2.

SO_x gases react with water in the atmosphere to form acids, and so their production is commonly associated with acid rain (which is an environmental issue addressed elsewhere).

Questions:

How are non-metal oxides formed?

What are the main anthropogenic (man-made) sources of NO_x compared to SO_x?

What are some of the main components of smog?

What gives smog its brownish color?

What are the two main factors that cause the concentrations of gases found in photochemical smog to fluctuate over time?

References:

https://en.wikipedia.org/wiki/NOx

https://openstax.org/books/chemistry-2e/pages/18-9-occurrence-preparation-and-compounds-of-oxygen

https://www.epa.gov/transportation-air-pollution-and-climate-change/smog-soot-and-local-air-pollution

https://en.wikipedia.org/wiki/Catalytic_converter

https://en.wikipedia.org/wiki/Sulfur_dioxide

NO_x and SO_x Learning Objective

Identify the sources of NO_x and SO_x gases and explain their importance in the formation of photochemical smog.

Acid Rain Learning Objective

Describe the definition of, sources of, consequences of, and solutions to, acid rain