

EWCE 105

ENVIRONMENTAL CHEMISTRY
Lecture – 8

Lecture Outlines

- Nitrogen Oxides (NO_x)
- Sulphur Oxides (SO_x)
- Photochemical Smog
- Lead

Nitrogen Oxides (NO_x)



- **Brownish gas** that hangs above large cities, is primarily nitrogen dioxide, NO_2.
- It forms from **the oxidation of nitric oxide, NO**, a **component of car exhaust**.

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

- Nitrogen Oxides (NO_x) includes : Nitric oxide (NO), Nitrogen dioxide (NO_2 – a criteria pollutant)

Two types of NO_x are formed during combustion:

1. Thermal NO_x : created when N and O in the combustion air are heated to high temperature (> 1000 K) to oxidize N.

Nitrogen Oxides (NO_x)

2. Fuel NO_x : result from oxidation of nitrogen compounds that are chemically bound in the fuel molecules themselves. Coal has about 3% N by weight; natural gas has almost none.

- Major Sources of Nitrogen Oxides (NO_x)

- Fuel combustion in stationary sources (power plants, heating plants).
- Vehicular emissions.
- Other sources e.g., industrial processes (nitric acid plants).

Effects of Nitrogen Oxides (NO_x)

- Almost **all NO_x emissions are in the form of NO**, which has **no known adverse health effects** at concentrations commonly found in air.
- NO can be oxidized to NO_2 ($NO + 0.5O_2 = NO_2$); **NO_2** may **react with hydrocarbon in the presence of sunlight to form "photochemical smog"**, which is **injurious**.
- **NO_2** also **reacts** with **Hydroxyl Radical (OH^o)** in the atmosphere to **form nitric acid (HNO_3),** which is washed out of the atmosphere as '**acid rain**'. It also forms "nitrate particles" in the atmosphere.
- **NO_2 irritates lungs**; persistent low level concentrations of **NO_2 increases respiratory illness**.
- **NO_2** can **cause damage to plants**; and **when converted to HNO_3**, it **leads to corrosion of metals**.

Sulfur dioxide

- Sulfur dioxide is a by-product of the burning of coal or oil.
- It reacts with moisture in the air to form sulfuric acid.
- It is primarily responsible for acid rain.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$
$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$$



$$CaCO_3(s) + H^+(aq) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq)$$

Sulfur Oxides (SOx) includes :

- Sulfur dioxide (SO_2 – criteria pollutant), and Sulfur trioxide (SO_3)

Formation of Sulfur Oxide (SO_x)

- Combustion of any S-containing material will produce SO_x;
- Oil and coal generally contain appreciable quantities of S (~ 0.5 to 6 %), either inorganic or organic form;
- When these fuels are burned, S is released mostly as SO_2, but also with small amounts of SO_3.

$$S + O_2 = SO_2$$
$$2SO_2 + O_2 = 2SO_3$$

- Once released SO_2 can be converted to SO_3 in a series of reactions involving free radicals such as OH^o.

$$SO_2 + OH\cdot = HOSO_2\cdot$$
$$HOSO_2\cdot + O_2 = SO_3 + HO_2\cdot$$

- SO_3 reacts quickly with H_2O to form H_2SO_4, which is the principal constituents of 'acid rain'.

$$SO_3 + H_2O = H_2SO_4$$

Formation of Sulfur Oxide (SO_x)

- H_2SO_4 molecules rapidly become particles by either condensing on existing particles in the air or by merging with water vapor to form H_2O-H_2SO_4 droplets.
- **Often a significant fraction of PM consists of Sulfate aerosols. Transformation of SO_2 to Sulfate particles is gradual, taking days.**
- Most Sulfate particles has an effective size of < 2 μm, with most of them being in the range of 0.2 to 0.9 μm. Their size is comparable to the wavelength of visible light, and thus their presence affects visibility. Their small size also allows deep penetration into the respiratory system.

Major Sources of Sulfur Oxides (SO_x)

- Natural processes e.g., volcanoes provide 67% of SO_x pollution across the globe
- Man-made / Anthropogenic sources contribute about 33% of SO_x pollution which is however, localized in some urban areas.

Man-made / Anthropogenic sources

- Fuel combustion in power plants and heating plants contributes the major part, accounting for about 80 % of all anthropogenic SO_x emission; combustion of coal being the primary source.
- Other industrial processes (e.g., copper manufacturing, petroleum refineries, sulfuric acid plants, cement manufacturing).
- Transportation contributes relatively little, because sulfur content of gasoline is relatively low.

Health Effects of Sulfur Oxides (SO_x)

- SO_2 is highly soluble and consequently is absorbed in the moist passage of upper respiratory system. Exposure to $SO_2 \sim 1$ ppm leads to constriction of the airways.

- SO_2, H_2SO_4 and Sulfates particles irritate mucus membrane of respiratory area and develop chronic respiratory diseases, e.g. bronchitis.

- The SO_2-Particulates (paralyzes the hair-like cilia, which line the respiratory tract) has been cited as a cause of death in several air pollution tragedies.

Effects of Sulfur Oxides (SO_x) on materials

- H_2SO_4 aerosols attack building materials, especially those containing carbonates, such as marbles and limestone. In the following reaction carbonate is replaced by sulfate, which is water soluble.

$$CaCO_3 + H_2SO_4 = CaSO_4 + CO_2 + H_2O$$

$CaSO_4$ formed in this way is gradually washed away by rain water, leaving pitted, discolored surface.

- Corrosion rate of most metals, especially iron, steel and nickel are accelerated by SO_x.

- H_2SO_4 mists can damage cotton and nylon. SO_x also damages paper and leather.

Control of Sulfur Oxides (SO_x) Pollution



Four possible approaches:

- Removal of SO_x from fuel gases.
- Use of low-sulfur fuels.
- Substitute of other energy sources for fuel combustion.
- Use of low-sulfur coal or minimize coal burning.

Photochemical Smog

When NOx, various Hydrocarbons (HCs, such as CH4) and Sunlight come together, they can initiate a complex set of reactions to produce a number of secondary pollutants known as "photochemical oxidants" or "photochemical smog".

It mainly occurs in highly motorized areas in large metropolitan cities.

NO_2+ HCs (e.g. CH_4) + Sunlight →Photochemical Smog

Cities that experience this smog daily include Los Angeles, Sydney, Mexico City, Beijing, and many more.

Formation of Photochemical Smog



Photochemical smog forms from a complex process, however the source of it is quite apparent.

- The largest contributor is automobiles,
- Coal-fired power plants, and
- Some other power plants also produce the necessary pollutants to facilitate its production.

Due to its abundance in areas of warmer temperatures, photochemical smog is most common in the summer.

Formation of Photochemical Smog

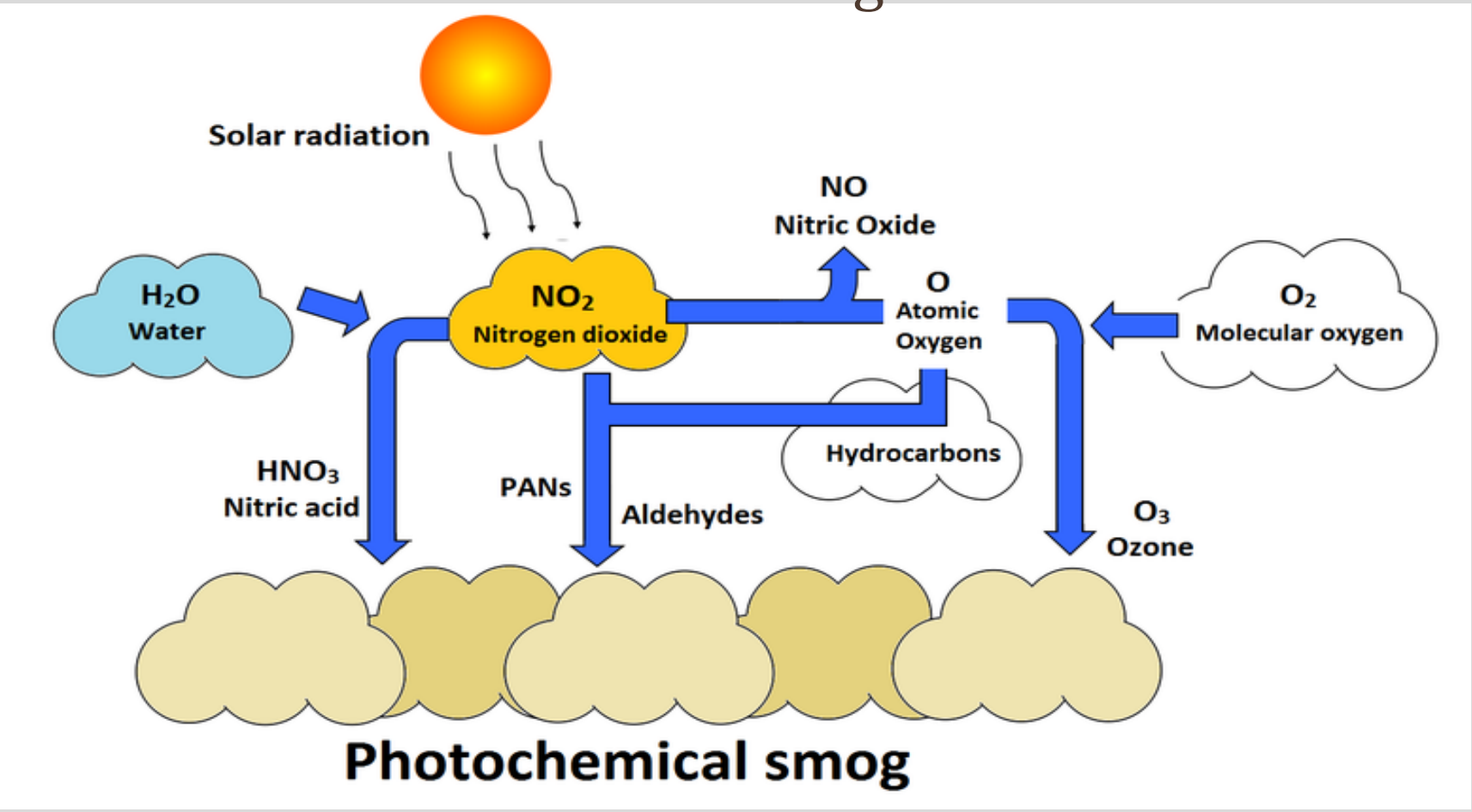
Steps of Photochemical smog formation:

Nitrogen oxides produced in the **car engine** are introduced **into the atmosphere**, which may **combine with water** to form **nitric acid or react with sunlight** to produce **singular oxygen atoms**, **which then combine** with **molecular oxygen to produce ozone**.

Composition of Photochemical Smog:

Nitric oxide (NO) and nitrogen dioxide (NO_2) emitted, when exposed to **ultraviolet radiation**, NO_2 goes through **a complex series of reactions with hydrocarbons to produce the components of photochemical smog**—a mixture of **ozone**, **nitric acid, aldehydes, peroxyacyl nitrates (PANs)** and other secondary pollutants.

Formation of Photochemical Smog



NO_2, ozone and PANs are called **photochemical oxidants** because they can react and oxidize certain compounds in the atmosphere

Simplified explanation of the chemistry of smog formation

Nitrogen dioxide (NO_2) can be broken down by sunlight to form nitric oxide (NO) and an oxygen radical (O):



Oxygen radicals can then react with atmospheric oxygen (O_2) to form ozone (O_3):



Ozone is consumed by nitric oxide to produce nitrogen dioxide and oxygen:



Simplified explanation of the chemistry of smog formation

Harmful products, such as PAN, are produced by reactions of nitrogen dioxide with various hydrocarbons (R), which are compounds made from carbon, hydrogen and other substances:

4) NO_2 + R → products such as PAN

The main source of these hydrocarbons is the VOCs. Similarly, oxygenated organic and inorganic compounds (RO_x) react with nitric oxide to produce more nitrogen oxides:

5) NO + RO_x → NO_2 + other products

Simplified explanation of the chemistry of smog formation

The significance of the presence of the VOCs in these last two reactions is dominant. Ozone is normally consumed by nitric oxide, as in reaction 3. However, when VOCs are present, nitric oxide and nitrogen dioxide are consumed as in reactions 4 and 5, allowing the build up of ground level ozone.

Health effects

Pollutant	Effects
Nitrogen oxides	• can contribute to problems with heart and lungs • links to decreased resistance to infection
Volatile organic compounds (VOCs)	• eye irritation • respiratory problems • some compounds are carcinogens
Ozone	• coughing and wheezing • eye irritation • respiratory problems (particularly for conditions such as asthma)
Peroxyacetyl nitrate (PAN)	• eye irritation • respiratory problems

Control of the occurrence of Photochemical Smog

The most effective way of reducing the amount of secondary pollutants created in the air is to reduce emissions of both primary pollutants.

Reduction of nitrogen oxide

- Use a process called '**catalytic reduction**'. A process which convert much of the nitric oxide from the engine exhaust gases to nitrogen and oxygen.

Reduction of VOCs

- Use of liquefied petroleum gas (LPG) or compressed natural gas (CNG) rather than petrol.

Lead

Source

- Most lead emission come from vehicles burning gasoline containing the **antiknock additive**, tetraethyl lead $(C_2H_5)_4Pb$.

Antiknock additives :

- An **antiknock agent** is a **gasoline additive** used **to reduce engine knocking** and increase the fuel's octane rating by raising the temperature and pressure at which auto-ignition occurs.

Lead is emitted to the atmosphere primarily in the form of inorganic particulates.

Human exposure to airborne lead primarily result from inhalation. It can also be ingested after lead has deposited onto foodstuff.

Lead

Adverse Effects

- About 1/3 of lead particles inhaled are deposited in the respiratory system, about ½ those are absorbed by bloodstream.
- Adverse impact of lead poisoning include aggressive, hostile and destructive behavioral changes, learning disabilities, severe and permanent brain damage and even death. Vulnerable groups include children and pregnant women.

Apart from Pb in road dust, other potential sources of Pb in Bangladesh can be paint, fabric and leather dyeing (hence textile and leather industries), metal smelters and battery industries.

Lecture Summary

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The End