Mission: To aware people of photochemical smog

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Abstract
Smog is a type of air pollutant. The word "smog" was coined in the early 20th century as a portmanteau of the words smoke and fog to refer to smoky fog. The burning of fossil fuels like gasoline can create another atmospheric pollution problem known as photochemical smog. We have discussed the sources of photochemical smog, chemistry of formation of photochemical smog, its adverse effects on the health as well as on the environment.

Keywords: photochemical smog, air pollutant, smog

1. Introduction
Photochemical smog is a condition that develops when primary pollutants (oxides of nitrogen and volatile organic compounds created from fossil fuel combustion) interact under the influence of sunlight to produce a mixture of hundreds of different and hazardous chemicals known as secondary pollutants. The Table below describes the major toxic constituents of photochemical smog and their effects on the environment.

Major Chemical Pollutants in Photochemical Smog: Sources and Environmental Effects

<table>
<thead>
<tr>
<th>Toxic Chemical</th>
<th>Sources</th>
<th>Environmental Effects</th>
<th>Additional Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Oxides (NO and NO2)</td>
<td>- combustion of oil, coal, gas in both automobiles and industry</td>
<td>- decreased visibility due to yellowish color of NO2</td>
<td>- all combustion processes account for only 5 % of NO2 in the atmosphere, most is formed from reactions involving NO</td>
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<td></td>
<td>- bacterial action in soil</td>
<td>- NO2 contributes to heart and lung problems</td>
<td>- concentrations likely to rise in the future</td>
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<td></td>
<td>- volcanic action</td>
<td>- NO2 can suppress plant growth</td>
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<td>- lightning</td>
<td>- decreased resistance to infection</td>
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<td>- may encourage the spread of cancer</td>
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<td>Volatile Organic Compounds (VOCs)</td>
<td>- evaporation of solvents</td>
<td>- eye irritation</td>
<td>- the effects of VOCs are dependent on the type of chemical</td>
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<tr>
<td></td>
<td>- evaporation of fuels</td>
<td>- respiratory irritation</td>
<td>- samples show over 600 different VOCs in atmosphere</td>
</tr>
<tr>
<td></td>
<td>- incomplete combustion of fossil fuels</td>
<td>- some are carcinogenic</td>
<td>- concentrations likely to continue to rise in future</td>
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<td></td>
<td>- naturally occurring compounds like terpenes from trees</td>
<td>- decreased visibility due to blue-brown haze</td>
<td></td>
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<tr>
<td>Ozone (O3)</td>
<td>- formed from photolysis of NO2</td>
<td>- bronchial constriction</td>
<td></td>
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<td></td>
<td>- sometimes results from stratospheric ozone intrusions</td>
<td>- coughing, wheezing</td>
<td></td>
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<td></td>
<td></td>
<td>- respiratory irritation</td>
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<td></td>
<td></td>
<td>- eye irritation</td>
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<td></td>
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<td>- decreased crop yields</td>
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<td></td>
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<td>- retards plant growth</td>
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<td></td>
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<td>- damages plastics</td>
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<td></td>
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<td>- breaks down rubber</td>
<td></td>
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<td>- harsh odor</td>
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<td>Peroxyacetyl Nitrates (PAN)</td>
<td>- formed by the reaction of NO2 with VOCs (can be formed naturally in some environments)</td>
<td>- eye irritation</td>
<td>- concentrations of 0.1 parts per million can reduce photosynthesis by 50 %</td>
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<td></td>
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<td>- high toxicity to plants</td>
<td>- people with asthma and respiratory problems are influenced the most</td>
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<td></td>
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<td>- respiratory irritation</td>
<td>- can only be formed during daylight hours</td>
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<td></td>
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<td>- damaging to proteins</td>
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</table>
**Development of Photochemical Smog**

Certain conditions are required for the formation of photochemical smog. These conditions include:

1. A source of nitrogen oxides and volatile organic compounds. High concentrations of these two substances are associated with industrialization and transportation. Industrialization and transportation create these pollutants through fossil fuel combustion.
2. The time of day is a very important factor in the amount of photochemical smog present. The following diagram illustrates the daily variation in the key chemical players. The diagram suggests:
   - Early morning traffic increases the emissions of both nitrogen oxides and VOCs as people drive to work.
   - Later in the morning, traffic dies down and the nitrogen oxides and volatile organic compounds begin to react forming nitrogen dioxide, increasing its concentration.
   - As the sunlight becomes more intense later in the day, nitrogen dioxide is broken down and its by-products form increasing concentrations of ozone.
   - At the same time, some of the nitrogen dioxide can react with the volatile organic compounds to produce toxic chemicals such as PAN.
   - As the sun goes down, the production of ozone is halted. The ozone that remains in the atmosphere is then consumed by several different reactions.
3. Several meteorological factors can influence the formation of photochemical smog. These conditions include
   - Precipitation can alleviate photochemical smog as the pollutants are washed out of the atmosphere with the rainfall.
   - Winds can blow photochemical smog away replacing it with fresh air. However, problems may arise in distant areas that receive the pollution.
   - Temperature inversions can enhance the severity of a photochemical smog episode. Normally, during the day the air near the surface is heated and as it warms it rises, carrying the pollutants with it to higher elevations. However, if a temperature inversion develops pollutants can be trapped near the Earth's surface. Temperature inversions cause the reduction of atmospheric mixing and therefore reduce the vertical dispersion of pollutants.
   - Inversions can last from a few days to several weeks.
4. Topography is another important factor influencing how severe a smog event can become. Communities situated in valleys are more susceptible to photochemical smog because hills and mountains surrounding them tend to reduce the air flow, allowing for pollutant concentrations to rise. In addition, valleys are sensitive to photochemical smog because relatively strong temperature inversions can frequently develop in these areas.

**Chemistry of Photochemical Smog**

The previous section suggested that the development of photochemical smog is primarily determined by an abundance of nitrogen oxides and volatile organic compounds in the atmosphere and the presence of particular environmental conditions. To begin the chemical process of photochemical smog development the following conditions must occur:

- Sunlight.
- The production of oxides of nitrogen (NOx).
- The production of volatile organic compounds (VOCs).
- Temperatures greater than 18 degrees Celsius.

If the above criteria are met, several reactions will occur producing the toxic chemical constituents of photochemical smog. The following discussion outlines the processes required for the formation of two most dominant toxic components: ozone (O3) and peroxyacetyl nitrate (PAN). Note the symbol R represents a hydrocarbon (a molecule composed of carbon, hydrogen and other atoms) which is primarily created from volatile organic compounds. Nitrogen dioxide can be formed by one of the following reactions. Notice that the nitrogen oxide (NO) acts to remove ozone (O3) from the atmosphere and this mechanism occurs naturally in an unpolluted atmosphere.

\[
\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2
\]

\[
\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{other products}
\]

Sunlight can break down nitrogen dioxide (NO2) back into nitrogen oxide (NO).

\[
\text{NO}_2 + \text{sunlight} \rightarrow \text{NO} + \text{O}
\]

The atomic oxygen (O) formed in the above reaction then reacts with one of the abundant oxygen molecules (which makes up 20.94% of the atmosphere) producing ozone (O3).

\[
\text{O} + \text{O}_2 \rightarrow \text{O}_3
\]

Nitrogen dioxide (NO2) can also react with radicals produced from volatile organic compounds in a series of reactions to form toxic products such as peroxyacetyl nitrates (PAN).

\[
\text{NO}_2 + \text{R} \rightarrow \text{products such as PAN}
\]

It should be noted that ozone can be produced naturally in an unpolluted atmosphere. However, it is consumed by nitrogen oxide as illustrated in the first reaction. The introduction of volatile organic compounds results in an alternative pathway for the nitrogen oxide, still forming nitrogen dioxide but not consuming the ozone, and therefore ozone concentrations can be elevated to toxic levels.

**Health effects**

Smog is a serious problem in many cities and continues to harm human health. Ground-level ozone, sulfur dioxide, nitrogen dioxide and carbon monoxide are especially harmful for senior citizens, children, and people with heart and lung conditions such as emphysema, bronchitis, and asthma. It can inflame breathing passages, decrease the lungs' working capacity, cause shortness of breath, pain when inhaling deeply, wheezing, and coughing. It can cause eye and nose irritation and it dries out the protective membranes of the nose and throat and interferes with the body's ability to fight infection, increasing susceptibility to illness. Hospital admissions and respiratory deaths often increase during periods when ozone levels are high.

**Levels of unhealthy exposure**

The U.S. EPA has developed an Air Quality Index to help explain air pollution levels to the general public. 8 hour average ozone concentrations of 85 to 104 ppbv are described as "Unhealthy for Sensitive Groups", 105 ppbv to 124 ppbv as "unhealthy" and 125 ppbv to 404 ppbv as "very unhealthy". The "very unhealthy" range for some other pollutants are: 355 μg m⁻³ - 424 μg m⁻³ for PM10; 15.5 ppm - 30.4ppm for CO and 0.65 ppm - 1.24 ppm for NO₂.
**Premature deaths due to cancer and respiratory disease**
The Ontario Medical Association announced that smog is responsible for an estimated 9,500 premature deaths in the province each year. A 20-year American Cancer Society study found that cumulative exposure also increases the likelihood of premature death from a respiratory disease, implying the 8-hour standard may be insufficient.

**Smog and the risk of certain birth defect**
A study examining 806 women who had babies with birth defects between 1997 and 2006, and 849 women who had healthy babies, found that smog in the San Joaquin Valley area of California was linked to two types of neural tube defects: spina bifida (a condition involving, among other manifestations, certain malformations of the spinal column), and anencephaly (the underdevelopment or absence of part or all of the brain, which if not fatal usually results in profound impairment).

**Smog and low birth weight**
According to a study published in The Lancet, even a very small (5 μg) change was associated with an increase (18%) in risk of a low birth weight at delivery, and this relationship held even below the current accepted safe levels.

**References**