

Photochemical Smog Pollution and Its Mitigation Measures

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ABSTRACT

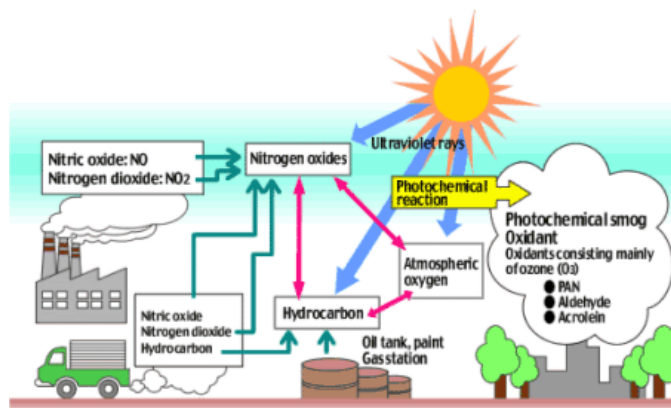
Photochemical smog is a unique type of air pollution. In the 1940s a new type of smog, known as photochemical smog, was first described in Los Angeles. Major Air Pollutants responsible for photochemical smog are carbon oxides (CO, CO₂), nitrogen oxides and nitric acid (NO, NO₂, HNO₃), sulphur dioxide and sulphuric acid (SO₂, H₂SO₄), suspended particulate matter (SPM), ozone (O₃), volatile organic compounds (VOCs). The reactions that lead to the formation of photochemical smog. Photochemical smog is a serious problem in many cities and continues to be harmful for senior citizens, children, and people with heart and lung conditions such as emphysema, bronchitis and asthma. Vegetation is easily harmed. Main agents of damage are ozone and PAN. Smog can also accelerate the deterioration of rubber, plastics, paints and dyes, damage to metals, stone, concrete, clothing, rubber and plastic is directly related to contaminants in the air. Photochemical ozone concentrations can be decreased by reduction in hydrocarbon and other VOC emissions and by reduction in NO_x but there is a non-linear (and sometimes inverse) dependence of ozone production on precursor emissions. Models have been developed to predict ozone concentrations and their response to different control measures.

Keywords: PAN; PAH; VOCs; HCs; NO_x; SPM; Hazards; Remediation; GHE.

1. INTRODUCTION

Air Pollution is defined as "Chemicals added to the atmosphere by natural events or human activities in high enough concentrations to be harmful". Two categories of air pollutant (1) Primary Air Pollutant: Harmful substance that is emitted directly into the atmosphere, (2) Secondary Air Pollutant: Harmful substance formed in the atmosphere when a primary air pollutant reacts with substances normally found in the atmosphere or with other air pollutants. The 20th century has been characterised by a transition from urban air dominated primary pollutants to one where secondary pollutants are very important. Three major outdoor air pollution problems are industrial smog from burning coal, photochemical smog from motor vehicle and industrial emissions, and acid deposition from coal burning and motor vehicle exhaust.

Smog the word "smog" is a portmanteau of smoke and fog. Modern smog is a type of air pollution derived from vehicular emission from internal combustion engines and industrial fumes that react in the atmosphere with sunlight to form secondary pollutants that also combine with the primary emissions to form photochemical smog. A new type of smog



known as photochemical smog was first observed in Los Angeles in the 1940s, Manila and Mexico City also experience this kind of smog. Many other cities in Greece, Israel, Japan, Australia, India and the UK have subsequently been found to suffer from photochemical smog. A photochemical smog is the chemical reaction of sunlight, nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in the atmosphere, which leaves airborne particles (called particulate matter) and ground-level ozone. Nitrogen oxides are released by nitrogen and oxygen in the air reacting together under high temperature

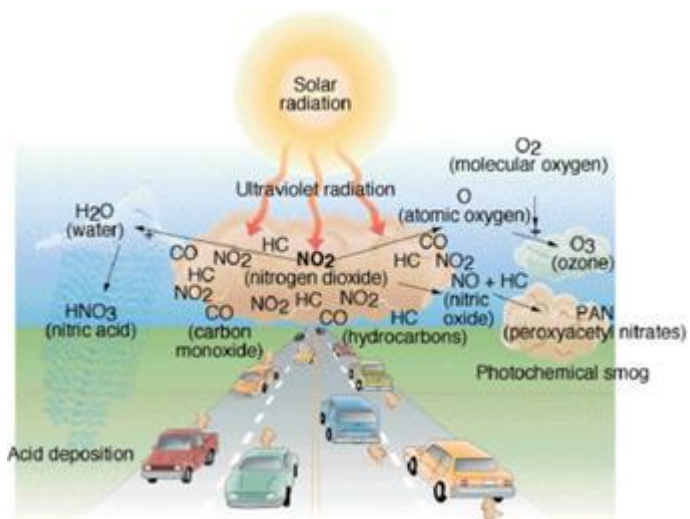
such as in the exhaust of fossil fuel-burning engines in cars, trucks, coal power plants, and industrial manufacturing factories. VOCs are released from manmade sources such as gasoline (petrol), paints, solvents, pesticides, and biogenic sources, such as pine and citrus tree emissions.

Photochemical smog is a unique type of air pollution which is caused by reactions between sunlight and pollutants like hydrocarbons and nitrogen dioxide. Although photochemical smog is often invisible, it can be extremely harmful, leading to irritations of the respiratory tract and eyes. In regions of the world with high concentrations of photochemical smog, elevated rates of death and respiratory illnesses have been observed. Photochemical smog is therefore considered to be a problem of modern industrialization. It is present in all modern cities, but it is more common in cities with sunny, warm, dry climates and a large number of motor vehicles. Because it travels with the wind, it can affect sparsely populated areas as well.

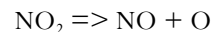
2. CAUSES OF PHOTOCHEMICAL SMOG

The initial step in photochemical reactions is the absorption of a photon by an atom, molecule, free radical or ion. The result of this absorption is strongly dependent on the energy, in other word the wavelength of the photon. Visible and ultraviolet portion of the light is required to start the photochemical reactions. The absorption can generate dissociation, internal rearrangement, fluorescence, or excited species. Photochemical smog can occur in any environment where there are large and continuous emissions of primary air pollutants. However specifics of climate and geography play an important role in the persistence and severity of the photochemical smog. Two factors influencing the formation of photochemical smog (a) Topography: Wind moves air masses both horizontally and vertically, dispersing pollutants and reducing concentrations with distance from the source. The amount of dispersion which occurs is directly related to the stability of the air or how much vertical air movement is taking place. (b) Temperature Inversion: Thermal inversions worsen any type of smog. It is abnormal arrangement of air masses. A warmer layer of air is trapped between two layers of colder air. This causes pollutants to be trapped near the earth's surface can form when hills or mountains stop horizontal winds, causing pollutants to collect over a city. Warm air collects over the polluted air, acting as a lid to stop the pollutants from being dispersed. Major Air Pollutants responsible for photochemical smog are Carbon oxides (CO, CO₂), Nitrogen oxides and nitric acid (NO, NO₂, HNO₃), Sulphur dioxide and sulphuric acid (SO₂, H₂SO₄), Particulates (SPM), Ozone (O₃), Volatile organic compounds (VOCs).

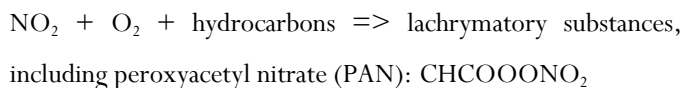
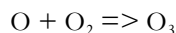
The reactions that lead to the formation of photochemical smog are irritated by sunlight and involve hydrocarbons and



nitrogen oxides emitted from automobiles. Photochemical smog (mainly automobile pollution) from the burning of coal and oil contains sulphur dioxide, sulphur trioxide, soot and ash (particulate matter) and sulphuric acid. It can cause breathing difficulties in humans, plus acid rain damage to plants, aquatic systems, and metal or stone objects. Nitric oxide (NO) is formed by the combustion of nitrogen-containing compounds (including fossil fuels) and by thermal fixation of atmospheric nitrogen. NO is then oxidized to nitrogen dioxide (NO₂) in the atmosphere. Nitrogen dioxide from automobile exhaust first absorbs sunlight and breaks down into nitrogen monoxide and reactive oxygen atom:



The oxygen atom reacts with other components of automobile exhaust (e.g. unburnt hydrocarbons) and those of the atmosphere (e.g. oxygen) in a series of complex reactions to produce a variety of lachrymatory and toxic chemicals (e.g. peroxyacetyl nitrate). Oxygen can be converted photochemically to small amounts of ozone (O₃). O₃ is a very reactive gas and can initiate other processes.



This noxious mixture of air pollutants can include the following:

- Aldehydes (RCHO)
- Nitrogen oxides, such as nitrogen dioxide
- Peroxyacetyl nitrates (PAN)
- Tropospheric ozone
- Volatile organic compounds (VOCs).

All of these chemicals are usually highly reactive and oxidizing. Photochemical smog is therefore considered to be a problem of modern industrialization. It is present in all modern cities, but

it is more common in cities with sunny, warm, dry climates and a large number of motor vehicles. Because it travels with the wind, it can affect sparsely populated areas as well.

3. FORMATION OF PHOTOCHEMICAL SMOG

Certain conditions are required for the formation of photochemical smog:

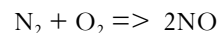
- (a) Ultraviolet Light; (b) Hydrocarbons; (c) Nitrogen oxides
Other conditions include:
- (1) Emission rates of the sources of nitrogen oxides (NO_x) and volatile organic compounds (VOC). High concentrations of these two substances are associated with industrialization and transportation, which create these pollutants through fossil fuel combustion.
 - (2) The time of day is a very important factor influencing on the amount of photochemical smog: (a) Early morning traffic increases the emissions of both nitrogen oxides and no methane hydrocarbons (NMHC) a type of VOCs - as people drive to work. (b) Later in the morning, traffic reduces and the nitrogen oxides and volatile organic compounds begin to react to form nitrogen dioxide and increase its concentration. (c) As the sunlight becomes more intense later in the day, nitrogen dioxide is broken down and its by-products from increasing concentrations of ozone. (d) At the same time, some of nitrogen dioxide can react with the volatile organic compounds to produce toxic chemicals such as PAN. (e) As the sun goes down, the production of ozone is stopped. The ozone that remains in the atmosphere is then consumed by several different reactions.
 - (3) Meteorological factors are important in the formation of photochemical smog. These conditions include: (a) Precipitation can reduce photochemical smog as the pollutants are washed out of the atmosphere with the rainfall. (b) Winds can transfer photochemical smog away, replacing it with fresh air. However, the problem may arise in distant areas that receive the pollution. (c) Temperature inversions can enhance the severity of a photochemical smog episode. If a temperature inversion is developed, the pollutants can be trapped near the Earth's surface. Inversions can last from a few days to several weeks. The atmosphere temperature directly affects the reaction rates and some emission rates.
 - (4) Topography is another important factor influencing on how severe a smog event can become. Communities situated in valleys are more susceptible to photochemical smog because the 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.

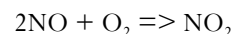
3.1. Formation of Nitrogen Oxides (NO_x)

The most natural way of forming nitrogen oxides [NO_x, where x may be 1 or 2] is lightning.

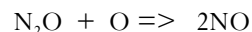
Atmospheric nitrogen reacts with nearby oxygen to form nitrogen monoxide.



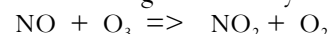
Nitrogen monoxide further reacts with oxygen to form nitrogen dioxide.



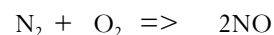
But this only generate limited amount of nitrogen oxides. In nature, nitrous oxide (N₂O) is produced by soil bacteria and oxidized to nitric oxide (NO) by atomic oxygen in the atmosphere:



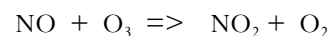
This is then oxidized to nitrogen dioxide by ozone.



High temperature combustion is an anthropogenic source of nitrogen dioxide. Nitrogen and oxygen, typically uncreative in nature, form nitric oxide at 1600 K:



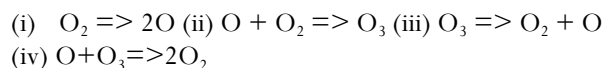
With subsequent oxidation by ozone to nitrogen dioxide in the atmosphere:



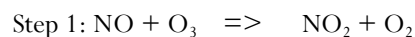
Sources of NO_x are equally split between mobile and stationary sources.

3.2. Formation of Ozone (O₃)

Ozone [O₃ (g)] is a pale blue gas (exists in the stratosphere of our atmosphere as the ozone layer). It is formed from atmospheric oxygen by the absorption of ultraviolet radiation of the right energy.



Thus, ozone is constantly created and destroyed. The above reaction is responsible for the vital screening effect of ozone. Ozone can also be formed in the lower part of the atmosphere. It is formed by reactions between nitrogen oxides and hydrocarbons under sunlight, or by electric sparks which occur in car engines or electrical appliances like photocopiers. In nature, the gas can be generated during lightning. Chemical reactions also occur between ozone and nitrogen, hydrogen, and chlorine. Small amounts of nitrogen oxides can destroy large amounts of ozone:



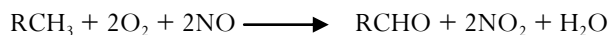
Now the NO can destroy more ozone.

3.3. Formation of Hydrocarbons

It is formed by reactions between nitrogen oxides and hydrocarbons under sunlight, or by electric sparks which occur in car engines or electrical appliances like photocopiers. In nature, the gas can be generated during lightning. Hydrocarbons have both the elements carbon and hydrogen. Motors of cars do not always burn the fuel completely. There are tiny amounts of unburnt hydrocarbons in car exhaust. Petrol and organic solvents are left unattended and exposed to air. Since those solvents are volatile in nature, these hydrocarbons pose danger to our health.

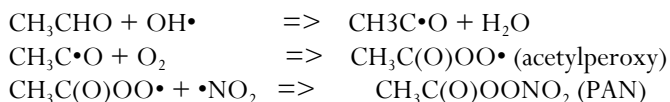
3.4. Formation of Particulates

Particulates make up smoke. They may be ashes from burning of fuels and Carbon-based molecules such as Aldehydes, Ketones and Hydrocarbons.

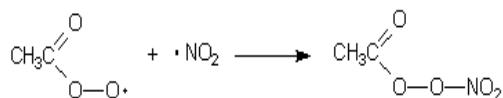
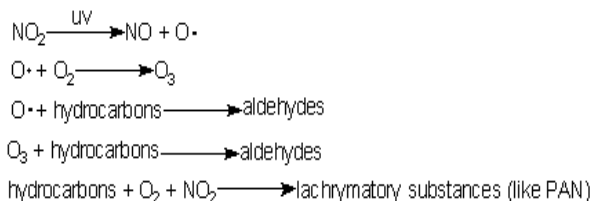


If fossil fuels (like coal and oil) are burnt, the tiny particles formed are mainly soot (carbon) from incomplete combustion. Incineration plants, factories and diesel vehicles are sources of emission. Incineration plants, factories and diesel vehicles are sources of emission.

3.5. Formation of Peroxyacetyl Nitrates (PAN)



4. HEALTH EFFECTS OF PHOTOCHEMICAL SMOG



Smog is a serious problem in many cities and continues to harm human health. Ground-level ozone, sulphur 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 and 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.

4.1. Effects on human health

4.1.1. Nitrogen Dioxides

- a. Eye and respiratory system irritants
- b. Damage to lung tissue

4.1.2. Sulphur Dioxide and Particulate material

Irritate respiratory tract and impair ability of lungs to exchange gases

4.1.3. Volatile organic compounds (VOCs)

- a. Global warming- Methane
- b. Carcinogenic- benzene
- c. Form Ozone

4.1.4. Ozone

Effects on human health: Low concentrations of ground-level ozone can irritate the eyes, nose and throat. As smog increases, it can trigger more serious health problems, including:

- a. Causes burning eyes, coughing, and chest discomfort
- b. Greater health threat to children than adults
- c. Air pollution can restrict lung development
- d. Children breathe more often than adults
- e. Children who live in high ozone areas are more likely to develop asthma
- f. As a result, diversity and population of some fresh water species will be reduced

4.1.5. Peroxyacetyl Nitrates (PAN)

PAN has been described as a highly oxidized unstable organic nitrogen compound which has been found to be a constituent of polluted atmospheres. Because of the toxic and irritating properties which PAN has been shown to have upon plants and human beings. It was postulated that the presence of PAN in the polluted photochemical atmosphere of large areas of California could contribute to a detrimental effect upon the cardio respiratory efficiency of human beings.

PAN is one of the most photo-toxic substances known damage includes cellular and biochemical changes with visible

leaf injury, leaf drop and decreased vigour and growth, and ultimately death. The classic injury caused by PAN is a glaze, followed by bronzing of the lower leaf surface there can be up to 50% loss in yield in citrus fruits, grapes, potatoes and tobacco and up to 30% in cotton as little as 0.05ppm of oxidant can cause significant effects.

4.2. *Effects on vegetation materials*

Vegetation is easily harmed main agents of damage are ozone and PAN. Sensitive crops, trees and other vegetation are harmed at lower ozone concentrations than is human health. Ground level ozone can damage leaves, and reduce growth, productivity and reproduction. It can cause vulnerability to insects and disease, and even plant death. When ozone levels are fairly high over a long period, agricultural crops can suffer significant harm.

The enhanced greenhouse effect

The pollutants emitted into atmosphere are implicated in numerous environmental problems. Ozone, for example, is not only a major component of smog; it also contributes to the enhanced greenhouse effect, which is predicted to lead to global climate change.

4.3. *Effects on materials*

Smog can also accelerate the deterioration of rubber, plastics, paints and dyes. Damage to metals, stone, concrete, clothing, rubber and plastic is directly related to contaminants in the air. The typical culprits are sulphur dioxide, sulphuric acid, ozone (photochemical smog), and nitric acid (HNO₃). Damage to crops and materials alone amounts to roughly \$10 billion dollars a year.

4.4. *Areas affected*

Smog can form in almost any climate where industries or cities release large amounts of air pollution, such as smoke or gases. However, it is worse during periods of warmer, sunnier weather when the upper air is warm enough to inhibit vertical circulation. It is especially prevalent in geologic basins encircled by hills or mountains. It often stays for an extended period of time over densely populated cities or urban areas, such as London, Atlanta, Houston, Phoenix, Las Vegas, New Delhi, New York, Cairo, Los Angeles, the Randstad or Ruhr Area and can build up to dangerous levels.

5. CONTROLLING THE FORMATION OF PHOTOCHEMICAL SMOG

Photochemical ozone concentrations can be decreased by reduction in hydrocarbon and other VOC emissions and by

reduction in NO_x. But there is a non-linear (and sometimes inverse) dependence of ozone production on precursor emissions have developed models to predict ozone concentrations and their response to different control measures. But there are problems with the variability in place and time of source and sink terms, with the transport and age of the air sample and with the formulation and detailed kinetics of the chemistry must assess the impact of a mixture of anthropogenic VOCs with widely different reactivity's must evaluate that impact in relation to ozone produced by biogenic hydrocarbons. Lean burning engines reduce NO_x, but create more CO and Hydrocarbons.

5.1. *Catalytic Converters: 3 Way Catalysts*

The present strategy is to reduce vehicle emissions by catalytic conversion of the exhaust gases typical converters consist of a layer of precious-metal (such as Pt or Rh) coated on an alumina substrate acts as a 3-way catalyst to convert:

1. NO to N₂
2. CO to CO₂
3. Hydrocarbons to CO₂ + H₂O

Conversion efficiency near 90% is possible for all three gases. But only if the air-to-fuel ratio is kept within strict limits (14.7 - 0.1):1 to maintain the correct ratio, an O₂ sensor is often provided in the exhaust flow with a feedback control signal to the fuel metering device.

5.2. *Diesel*

The emissions of unburned hydrocarbon and CO are markedly better from diesel-powered cars NO_x emissions are only marginally worse than those from gas cars with efficient catalytic converters however, they have increased particle emissions.

5.3. *Biodiesel*

Recently, biofuels have been the focus of attention as a possible means of reducing greenhouse gas emissions and noxious urban emissions from transport.

5.4. *Hydrogen and Electricity*

H₂-powered and electric vehicles are cleaner on the road. H₂ produces water, and electric cars have no emissions at all however, the pollution audit must include emissions due to the generation of the H₂ or of the electricity.

5.5. *Lifestyle Changes*

Small decreases in legal speed limits not only conserve fuel, but significantly reduce NO_x emissions with a negligible

increase in hydrocarbon. Increased uses of public transportation also reduce photochemical smog.

5.6. Polycyclic Aromatic hydrocarbons (PAHs)

PAHs are caused by incomplete combustion anthropogenic sources include motor vehicles, (both diesel and gas), stationary power plants (coal and oil), domestic (coal and wood burning, tobacco smoke), as well as deliberate biomass burning. The compounds are ubiquitous in the atmosphere a small contribution to the atmospheric load of PAHs may come from natural sources such as forest fires or volcanoes, but the predominant sources are anthropogenic important due to their impact on human health.

6. THE FUTURE

Even as smog is being reduced in large cities, and over entire regions such as the east and west coasts, it is growing in formerly pristine spots such as Cape Cod and the Great Smokies. This shows that pollution can travel great distances and still be a problem, and that regional solutions to regional problems will have to be found. For example, it has been reported that some 30 species of plants in the Great Smoky Mountains National Park are dying out or have been seriously damaged because of ozone and acid rain.

Another ray of hope is the development of a replacement for perchloroethylene, then solvent used in dry cleaning that releases vapor to the air. Perchloroethylene, in addition to being a VOC implicated in air pollution, is a groundwater contaminant and may cause cancer and so dry cleaners must treat the solvent as hazardous waste. The hydroxyl radical cleans the atmosphere, and of course, the more polluted the air is, the more demand there is for the hydroxyl radical to clean it. The attack on dirty air may involve unanticipated benefits. Enforcement of more Environmental Protection Laws, Reduction of primary pollutants (NO_x and VOCs), NO_x-catalytic converters in vehicles and industries may be considered. VOC more than 700 chemicals found released by VOCs. Reductions in emissions of SO₂ and VOCs mean a relative increase in UV-absorbing aerosols such as SO₂, mineral dust and soot, and such particulates apparently inhibit smog production, so there is a positive feedback loop.

There is some concern that the developing countries will follow the path taken by the industrialized countries and create high pollution levels in the pursuit of economic development, but the problem may be more acute in those countries because of their economic dependence on agriculture.

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