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Studies on the urban air pollution caused by photochemical smog

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Abstract
Unburned hydrocarbons pollute the urban air due to result of uncompleted combustion and the evaporation of solvents and liquid fuels. Volatile organic compounds (VOCs) and other organic substances including hydrocarbons are readily vaporized. Free radicals are added in the urban air with major reactive hydrocarbons which contain a C = C bond. Warmth, ample sunlight, and a stagnant of air are also required for the formation of the Photochemical Smog. Nitrogen dioxide (NO_2), ozone (O_3), PAN (per-oxy acetyl nitrate), and chemical compounds that contain the –CHO group (aldehydes) are the major undesirable components of photochemical smog. Major cities in the World are subjected to smog. The cities are the obvious substantial sources for the emission of sufficient NOx, different hydrocarbons and other volatile organic compounds into air. Smog makes some plant damage, health hazards, and eye irritations to human beings if their concentrations are sufficiently high.

Keywords: PAN (Per-oxy acyl nitrate), photochemical smog, volatile organic compounds, health hazards, free radicals

Introduction
The clarity of the sky is obscure by the dust, smoke and other dry particulate matters, which are actually meant as Haze. There are different codes of different categories of fog, dust, mist, ice fog, steam fog, haze, smoke, volcanic ash and snow. Farming, traffic, industry and wildfires are the different sources of haze particles [1]. Haze may appear as brownish or bluish, and mist tends to bluish grey, depending on the direction of view with respect to the Sun. Dry air forms haze, whereas humid air forms mist. Wet haze is a form of haze, whereby haze particles act as condensation nuclei for the formation of mist droplets.

The word haze is generally meant for visibility-reducing aerosols of the wet type. Aerosols are formed in the atmosphere by the complex chemical reactions between sulphur di-oxides, emitted during combustion and thus converted into sulphuric acid. In presence of sunlight, high relative humidity and stagnant air flow enhance these chemical reactions. There is another small component of wet-haze aerosols as terpenes, released by trees. Therefore, wet haze is a phenomenon of summer season. Smog is the type of air pollution, derived from vehicular emission from industrial fumes and combustions of engines. These atmospheric pollutants react with sunlight and primary emissions, to form photochemical smog. Photochemical smog refers to the atmospheric condition which becomes hazy with a poor visibility due to formation of various secondary pollutants or aerosols in atmosphere by photochemical reactions, preferably in metro-politan cities. A typical brownish gray haze formed by the action of solar ultraviolet on atmosphere, which is polluted with hydrocarbons and nitrogen oxides. In the bright sunlight, nitric acid, organic compounds, ozone and other anthropogenic air pollutants are getting trapped at the ground level [2]. The pollutants have some detrimental effects on plants as well as on human being. Photochemical smog often have an unpleasant odour due to some of its gaseous components. Smog is the word which is represent as a haze near the ground made by a combination of different air pollutants. Photochemical smog was first observed in Los Angles, USA, in mid 1940s. Then these incidents have been detected in major cities in the world. The word -SMOG‖ has been derived from smoke and fog. This develops a hazy weather condition with poor visibility with formation of aerosols in atmosphere by photo dissociations and photo reactivations.

Since 2002, smog severity is often provoked by straw burning in neighboring agricultural areas. The ground pollution level of Los Angles, Beijing, Delhi, Lahore, Mexico City, Tehran are often increased by inversion [4]. Smog is hazardous to human health, can cause severe sickness, respiratory discomfort, shortened life span or premature death [3]. In India, major metropolitan cities are ideal candidates for formation of photochemical smog.

Conditions for formation of smog

- Air stagnation
- Abundant sunlight
- High concentration of hydrocarbon and nitrogen oxides in the atmosphere.

Causes: Exhausts of automobiles and major stationary sources perform some photochemical reactions in the lower atmosphere by the interaction of hydrocarbons and nitrogen oxides, create Smog. These in turn results in a series of complex reactions producing different secondary pollutants, some photo-oxidants as ozone's, aldehydes, ketones and per-oxy acyl nitrates (PANs). Ozone in the stratosphere protects us against harmful ultraviolet radiation, but on the ground, it is hazardous to human health.
The emission of nitrogen oxides from internal combustion engines into the air creates photochemical smog. Some chemical reactions occur between free atoms of oxygen (O) and molecular oxygen (O2) to form the ozone by absorbing visible or ultraviolet sunlight [2]. Smog formation is totally depending on the chemical reaction of some hydrocarbons, organic compounds and sunlight.

Mechanism of smog formation

In a typical smog formation:
The starting mechanism is absorption of UV light from Sun by NO_2, which then decomposes into nitric oxide (NO) and highly reactive oxygen atom (O).

$NO_2 + UV = NO + O$

Reactive oxygen atom (O) combines with molecular oxygen (O_2), to form ozone (O_3) which itself is reactive and act as an oxidant. An energy absorbing molecule or particle required stabilizing ozone or else it will rapidly decompose.

$O + O_2 + M = O_3 + M$
$O_3 + NO = NO_2 + O_2$

But NO in presence of hydrocarbons (HC) in atmosphere reacts with hydrocarbon radical per-oxy acyl (RCO_3.), as a result O_3 concentration builds up to dangerous levels.

HC + O = RCO. (Acyl radical)
$RCO + O_2 = RCO_3$. (Per-oxy acyl radical)
RCO_3 + HC = RCHO (Aldehydes) and R_2CO (Ketones)
$RCO_3 + NO = RCO_2 + NO_2$
$RCO_3 + O_2 = RCO_2 + O_3$
$RCO_2 + NO = RCO + NO_2$

Thus, the NO level, that builds up during night and early morning when there is heavy commuter traffic, drops off eventually later in the day with a concomitant increase of NO_2 and O3 levels in atmosphere. Increased NO_2 concentration initiates reaction with RCO_3 to form per-oxy acyl nitrates (PANs).

$RCO_3 + NO_2 = RCO_3NO_2$ (PAN)

Three of the common members of PAN families are:
a) Per-oxy formyl nitrate (PFN)
b) Per-oxy acetyl nitrate (PAN)
c) Per-oxy benzoyl nitrate (PB_2N)

However, CO and SO_2 also play significant role in smog formation:

$CO + O_2 + NO = CO_2 + NO_2$
$SO_2 + HO_2 = OH + SO_3$

SO_3 in turn is converted to H_2SO_4 droplets resulting in the formation of a haze.

Smog behavior

Formation of photochemical smog is a dynamic process. In the morning, the NO and HC levels are increased followed quickly by increase in NO_2. NO_2 reacts with sunlight leading to various skin reactions and ultimately to the production of O_3 and other oxidants. O_3 concentrations increase until (sometimes in afternoon) it reaches a maximum and then decreases gradually. NO_2 concentrations diminish from its peak as O_3 concentration builds up and is usually low by late afternoon. The typical episode occurs in hot, sunny weather under low humidity conditions.

Effects of "SMOG"

- Characteristics symptoms of smog are the brown haze in atmosphere with reduced visibility.
- Human health is affected primarily by oxidant species (O_3), PAN, NO_2 and aerosols (containing sulphates, nitrates and ammonium ions)
- Impairment of physical performances at oxidant level (O_3, PAN) above 0.15 ppm.
- Attacks in asthmatics increases at 0.25 ppm.
- Chest pain, cough and headache are reported at a concentration range of 0.25 to 0.30 ppm.
- Eye irritation, as PAN is a powerful lachrymator at 0.1 to 0.45 ppm.
- Respiratory distress, extreme fatigue and lack of coordination have been observed.
- Plant damage occurs as PAN and O_3 are one of the most phytotoxic substances at 0.05 ppm level.
- Complications arise in respiration from the indoor environment and on inhalation of fungi from roof thatch or smoke, when there is no room chimney. Respiratory complications arising from space heaters or gas ovens, inhalation of tobacco smoke in indoor environment by non-smokers, leads to lung cancer.
- Northern India has been covered in a thick layer of winter smog since last few years [11]. The situation has fallen drastically in capital, New Delhi, where particulate matters i.e. very fine dust particles and toxic gases are concentrated in the stagnant air.
- In India, among various cities, New Delhi is the most polluted one and this air pollution may cause death of about 10,500 people every year. In the year 2013, Delhi pollution was increased by 44% for these peak levels of particulate matter (PM) due to high vehicular and industrial emissions, construction work and crop

burning. The airborne particulate matter, PM 2.5 is considered as the most harmful one and hazardous to human health with 153µgms [9]. Delhi people specially women and children are supposed to be more affected due to rising of these pollution level with asthma or lung cancer [5]. During winter season, Delhi weather becomes almost dull of smog, results in the rail and traffic disruption every year [7]. Since 1998, Delhi has faced a severe problem with its average maximum temperature declining due to rising of the air pollution and smog [6].

- Delhi residents are mostly unaware about its alarming pollution level in the city and health issues associated with this pollution. Delhi has already taken some urgent measures to curb pollution, as Delhi has enormous quantity of trees and Delhi Transport Corporation operates environment friendly Compressed Natural Gas (CNG) buses since mid-1990s. In 1996, a litigation had been started in the Supreme Court of India by Centre for Science and Environment (CSE) for public interest, that ordered the conversion of buses and taxis to run on CNG and banned the use of petrol in 1998 [6]. In the year 2003, Delhi won the first 'Clean Cities International Partner of the Year' award by United States Department of Energy's for its "bold efforts to curb air pollution and support alternative fuel initiatives". Furthermore, a credit also goes to Delhi Metro for significantly reducing air pollutants in the city [8].
- Stubble burning and rise in market share of diesel cars have been creating high pollution since many years which causes the formation of smog [10]. Burning of agricultural waste in nearby Punjab, Haryana and Uttar Pradesh regions results in severe intensification of smog over Delhi, stated by CUE and System of Air Quality Weather Forecasting and Research (SAFER). An environmental panel has appealed to India's Supreme Court to impose a 30% cess on diesel cars and the state government of adjoining Uttar Pradesh is considering imposing a ban on crop burning to reduce pollution in Delhi NCR [12, 13].

Control

Control of photochemical smog requires:

- Primary emission reduction.
- Nitrogen oxides reduction in a substantial amount produced in urban areas.
- To restrict the release of hydrocarbons from different mobile and stationary sources. Use of catalytic converters in auto exhausts, regular maintenance and decrease in legal speed limits reduce NOx emission.
- Use of fuels such as hydrogen and methanol eliminates HC problem.

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