ENVIS NEWSLETTER

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AIR POLLUTION CHEMISTRY - 1

CRITERIA POLLUTANTS- GASEOUS

ENVIS NEWSLETTER

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Editorial

Environment is the essential component of human life on which all living things depends for survival. There is a continuous interaction going on in each component of Earth system, change in one component affects the functioning of other either in positive or negative way and hence unsustainable use of natural resources during past few decades disturbs the functioning of Earth's ecosystem and alter the normal composition of Earth's atmosphere significantly. This result in the severe problems like acid rain, global warming, climate change, biodiversity loss, air pollution etc. and place the striking problems like food security, energy security, unpredictable weather in front of human race. To tackle these issues one need to know the present scenario of our atmosphere and how it changed over period of time; also the knowledge of major components which are responsible for this alteration is important. In view of these we are writing the series of ENVIS newsletters under the heading of "Air Pollution Chemistry" which will starts by giving you the basic information of our atmosphere, its normal composition, anthropogenic drivers of air pollution, climate change, and ends by conveying you there effects on our environment.

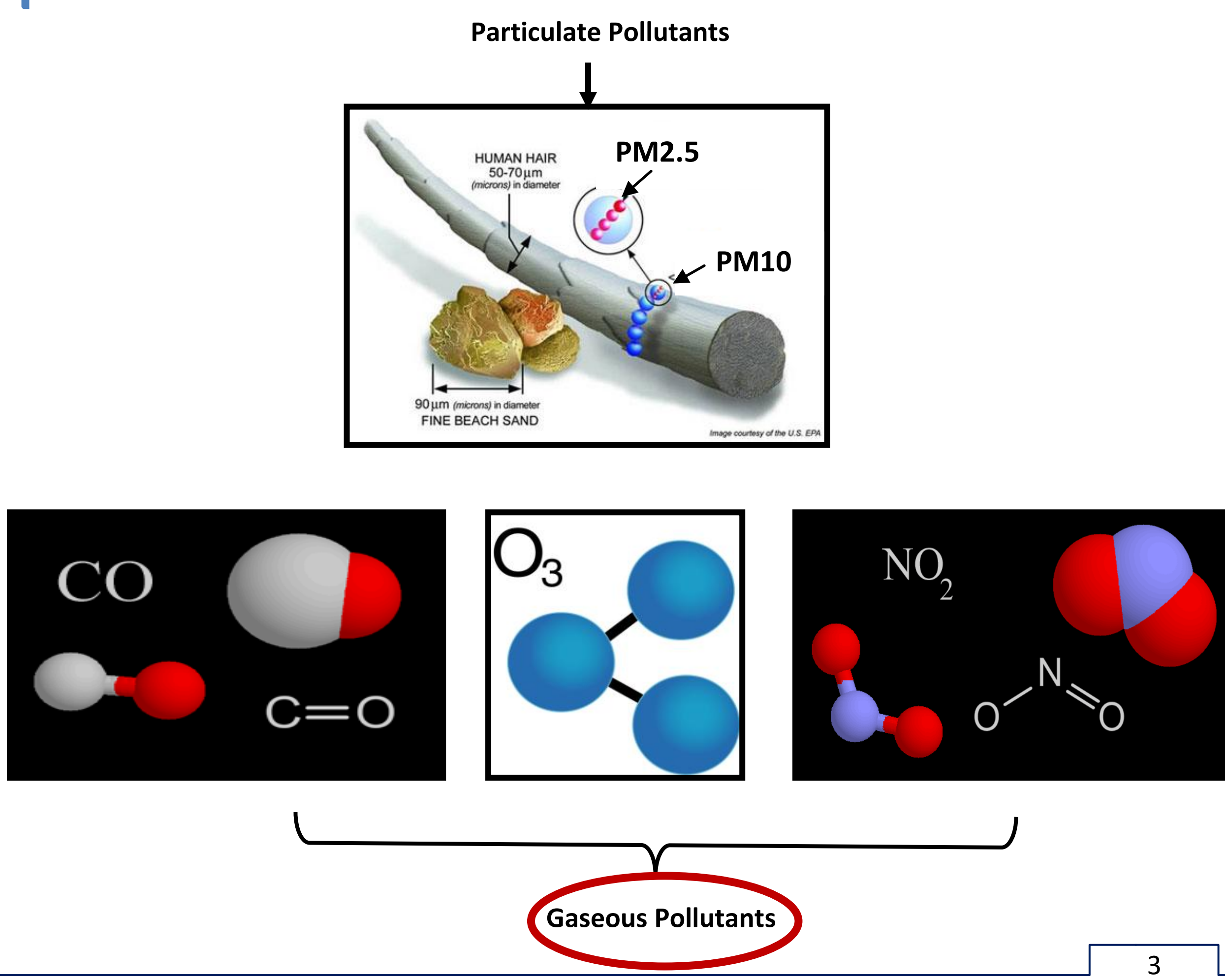
Present issue gives you detailed information regarding O3, CO and NO2, important criteria pollutants, which on elevated concentrations shows adverse effect on human health. We hope our attempt to convey complicated scientific information in simple language will help to create awareness amongst the common public which is the first step towards safeguarding our environment.

Criteria Pollutants

The five commonly found air pollutants in the atmosphere are particulate matter (PM), ground-level ozone (O_3), carbon monoxide (CO) and nitrous oxides (NO_X). Environment Protection Agency (EPA) identified these pollutants as "criteria" air pollutants because they can harm health and the environment.

It is evident from the medical records that short term exposure to these pollutants show immediate symptoms like coughing, eye and respiratory tract irritation, difficulty in breathing, headache, dizziness, visual disorders and memory impairment. Besides this prolonged exposure to these pollutants adversely affect lung, heart and brain functioning causing diseases like asthma, lung cancer, chronic respiratory disease, acute respiratory symptoms, decreased lung function, soreness of the nasopharynx and lungs etc. Hence study of these pollutants become important to reduce the associated health risk.

CRITERIA POLLUTANTS



Ozone (O_3)

What is Ozone?

Ozone is a tri-atomic molecule, constituting of three oxygen atoms. It formed from di-oxygen by the action of Ultraviolet radiation and atmospheric electrical charges. Ozone normally occurs in gaseous state at two locations in atmosphere one at stratosphere and at troposphere near ground level. But at which place Ozone is "Good" and where it is "Bad" for your health and environment?

How Can Ozone Be Both Good and Bad?

In troposphere near ground level Ozone is considered as a potent pollutant showing adverse effect on crops, vegetables, human health and also it's a main ingredient of urban smog. Whereas at Stratosphere the same Ozone acts as a life protecting guard, it absorbs biologically harmful UV radiations and protects life on Earth.

Ozone as Protector

Ozone in the stratosphere is produced from the reaction between short-wave ultraviolet radiation and Oxygen:

Here it absorbs biologically harmful ultraviolet (UV) radiation coming from the sun

O_2 + photon (radiation < 240 nm) → 2 O

$O + O_2 + M \rightarrow O_3 + M$

Where "M" denotes the third body that carries off the excess energy of the reaction.

O3 produced during this reaction is destroyed by the reaction with atomic oxygen:

$O_3 + O \rightarrow 2\ O_2$

The latter reaction is catalyzed by the presence of certain free radicals, of which the most important are hydroxyl (OH), nitric oxide (NO) and atomic chlorine (Cl) and bromine (Br).

Depletion of Ozone Layer

In recent decades the amount of ozone in the stratosphere has been declining mostly because of emissions of various Ozone Depleting Substances **(ODS)** including chlorofluorocarbons (CFCs), hydro chlorofluorocarbons (HCFCs), halons, methyl bromide, carbon tetrachloride, methyl chloroform and other chlorinated and brominated substances.

Higher emissions of these compounds results in the increased concentration of Ozone depleting catalysts as compared to their background concentration. Once released into the air these ODS degrade very slowly. In fact, they can remain intact for years as they move through the troposphere until they reach the stratosphere. There they are broken down by the intensity of the sun's UV rays and release chlorine and bromine molecules, which destroy the good ozone. Scientists estimate that one chlorine atom can destroy 100,000 "good" ozone molecules.

These substances were extensively used during the past for verities of reasons, coolants, foaming agents, fire extinguishers, solvents, pesticides, and aerosol propellants. Although we have reduced or eliminated he use of many ozone-depleting substances, their use in the past can still affect the protective ozone layer. Scientists estimate that one chlorine atom can destroy 100,000 "good" ozone molecules.

Research indicates that depletion of the good ozone layer is being reduced worldwide. Thinning of the protective ozone layer can be observed using satellite measurements, particularly over the Polar Regions.

Ozone as a Pollutant

Ground-level ozone is a pernicious secondary air pollutant, toxic to both humans and vegetation. It is formed at the surface by oxidation of VOCs and carbon monoxide in the presence of NO_x. The mechanism is complicated, involving hundreds of chemically interactive species to describe the VOC degradation pathways. A simple schematic is as bellow:

$VOC + OH \rightarrow HO_2 + \text{other products}$

$HO_2 + NO \rightarrow OH + NO2$

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

Nitrogen Dioxide (NO_2)

What is NO_x?

NO_x is a generic term for mono-nitrogen oxides NO and NO_2 (nitric oxide and nitrogen dioxide). They are produced from the reaction of nitrogen and oxygen gases in the air during combustion, especially at high temperatures.

Formation and reactions of NOx

During any combustion process NO_x is formed. In atmospheric chemistry, NOx represents the total concentration of NO and NO_2 (NOx= NO+NO2)

The oxygen and nitrogen do not react at ambient temperatures. But at high temperatures, they have an endothermic reaction producing various oxides of nitrogen. Such temperatures arise inside an internal combustion engine or a power station boiler, during the combustion of a mixture of air and fuel.

In the presence of excess oxygen (O_2), nitric oxide (NO) reacts with the oxygen to form nitrogen dioxide (NO_2). During daylight, the concentrations of NO and NO2 is found in equilibrium; the ratio NO/NO_2 is determined by the intensity of sunshine (which converts NO_2 to NO) and the concentration of ozone (which reacts with NO to again form NO_2).

When NO_x and volatile organic compounds (VOCs) react in the presence of sunlight, they form photochemical smog, a significant form of air pollution, especially in the summer also its responsible for the formation of acid rain.

Formation of nitric acid and acid rain

Mono-nitrogen oxides eventually form nitric acid when dissolved in atmospheric moisture, forming a component of acid rain. The following chemical reaction occurs when nitrogen dioxide reacts with water:

$$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

Nitrous acid then decomposes as follows:

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$$

where nitric oxide will oxidize to form nitrogen dioxide that again reacts with water, ultimately forming nitric acid:

$$4\ NO + 3\ O_2 + 2\ H_2O \rightarrow 4\ HNO_3$$

Mono-nitrogen oxides are also involved in tropospheric production of ozone.

This nitric acid may end up in the soil, where it makes nitrate, where it is of use to growing plants.

Carbon Monoxide (CO)

Carbon monoxide is a colorless, odorless and tasteless gas which is a by-product of the incomplete burning of fuels. Worn or poorly adjusted and maintained combustion devices (e.g., boilers, furnaces), exhaust from automobiles are the significant sources of NOx.

Role in ground level ozone formation

Carbon monoxide is, along with aldehydes, part of the series of cycles of chemical reactions that form photochemical smog. It reacts with hydroxyl radical (OH) to produce a radical intermediate HOCO, which transfers rapidly its radical hydrogen to O_2 to form peroxy radical (HO_2) and carbon dioxide (CO_2). Peroxy radical subsequently reacts with nitrogen oxide (NO) to form nitrogen dioxide (NO_2) and hydroxyl radical. NO_2 gives O via photolysis, thereby forming O_3 following reaction with O_2. Since hydroxyl radical is formed during the formation of NO_2, the balance of the sequence of chemical reactions starting with carbon monoxide and leading to the formation of ozone is

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$$

(Where hv refers to the photon of light absorbed by the NO_2 molecule in the sequence)

Although the creation of NO_2 is the critical step leading to low level ozone formation, it also increases this ozone in another, somewhat mutually exclusive way, by reducing the quantity of NO that is available to react with ozone.

Health Effects of NO2 , O3 and CO

NO_x reacts with ammonia, moisture, and other compounds to form nitric acid vapor and related particles. Small particles can penetrate deeply into sensitive lung tissue and damage it, causing premature death in extreme cases. Inhalation of such particles may cause or worsen respiratory diseases, such as emphysema or bronchitis, or may also aggravate existing heart disease. NO_x readily reacts with common organic chemicals, and even ozone, to form a wide variety of toxic products: nitroarenes, nitrosamines and also the nitrate radical some of which may cause biological mutations.

Recently another pathway, via NO_x, to ozone has been found that predominantly occurs in coastal areas via formation of nitryl chloride when NO_x comes into contact with salt mist.

Ozone can cause adverse effects such as damage to lung tissue and reduction in lung function mostly in susceptible populations (children, Asthmatics). Ozone can be transported by wind currents and cause health impacts far from the original sources.

Carbon monoxide is an extremely poisonous gas. Breathing air that contains as little as 0.1% carbon monoxide by volume can be fatal; a concentration of about 1% can cause death within a few minutes. Early symptoms of carbon monoxide poisoning include drowsiness and headache, followed by unconsciousness, respiratory failure, and death.

Carbon monoxide enters the bloodstream through the lungs and reduces oxygen delivery to the body's organs and tissues. The health threat from carbon monoxide at low levels is most serious for those who suffer from cardiovascular disease, such as angina pectoris. At much higher levels

These pollutants are also responsible for formation of smog. Children, people with lung diseases such as asthma, and people who work or exercise outside are particularly susceptible to adverse effects of smog such as damage to lung tissue and reduction in lung function.

DO YOU KNOW?

In 2009, nitrous oxide (N_2O) was the largest ozone-depleting substance emitted through human activities

The ozone layer was discovered in 1913 by the French physicists Charles Fabry and Henri Buisson. Its properties were explored in detail by the British meteorologist G. M. B. Dobson, who developed a simple spectrophotometer (the Dobsonmeter) that could be used to measure stratospheric ozone from the ground. Between 1928 and 1958 Dobson established a worldwide network of ozone monitoring stations, which continue to operate to this day. The "Dobson unit", a convenient measure of the columnar density of ozone overhead, is named in his honor.

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