ISBN: 978-93-90847-02-0

11. Volatile Organic Compounds (VOCs): An Overview

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Abstract:

Volatile organic compounds (VOCs) are the organic compounds that evaporate very easily and are dangerous for the atmosphere. VOCs may be either naturally occurring or man-made. They are warmed up due to human activities like industrialization, aerosol sprays etc.

There are several and they pose a great danger to human beings. VOCs are common in modern life, from the paint on walls to the gases emitted by cars. Because these gases evaporate easily and accumulate in the atmosphere, they contribute a great deal to urban heat island effect. In the present Chapter, attempts have been made to assess the role of VOCs as a major contributor to air pollutants. We have discussed their role in atmospheric chemistry, measurement challenges and methods to control them in air.

11.1 Introduction to VOCs:

Many of the most common air pollutants created by chemical and petrochemical industries are Volatile Organic Compounds (VOCs). Volatile organic compounds (VOCs) are chemicals that slowly evaporate at room temperature i.e., these compounds possess high vapour pressure. Organic compounds are defined as any compound containing carbon. In addition to carbon, other elements may be present in the compound. Organic compounds may contain hydrogen, halogens (e.g., chlorine, fluorine or bromine), oxygen, sulphur, phosphorus, silicon, or nitrogen. The only exception is carbon oxides and inorganic carbonates and bicarbonates.

VOCs can be either gaseous or liquid and belong to a variety of chemical classes, including alkanes, alkenes, and cyclic hydrocarbons. VOCs are used in many industrial applications, including coatings, adhesives, cleaning supplies, paints. One source of VOC chemicals in this industry is electric arc furnaces.

Typically, these VOC chemicals do not pose a serious threat to the environment. However, due to certain properties of these chemicals, if released into the atmosphere they contribute directly to air pollution and global warming. For example, some volatile organic solvents that are used in certain installations also produce ozone precursors which can react with oxides of nitrogen in presence of sunlight and consequently, produce greenhouse gases which harms the ozone layer.

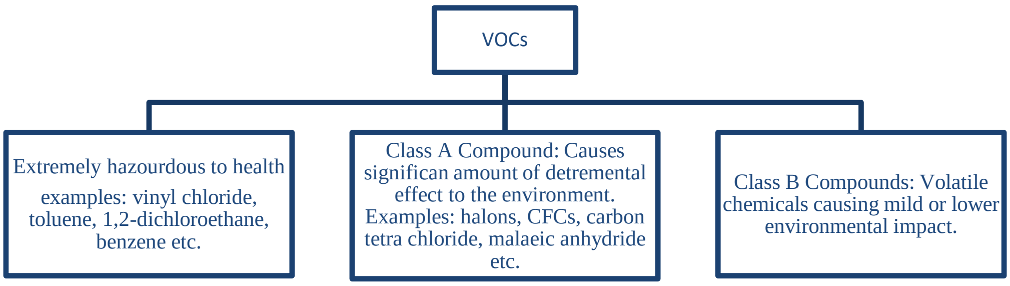
The side effects of volatile organic compounds on human health can consist of respiratory system diseases, cardiovascular and gastrointestinal diseases, eyesight problems and skin diseases. Volatile organic compounds are hepatotoxic, nephrotoxic, neurotoxic and carcinogen.

Of serious environmental concern are volatile organic compounds (VOCs) because of the harmful properties that they exhibit in varying degrees. These harmful effects can be summarized as follows:

- Cause direct toxicity to human health
- involvement in photochemical ozone generation at ground level, with consequent detrimental effects
- depletion of stratospheric ozone
- contribution to global climate change

11.2 Classification of VOCs on the Basis of its Harmfulness:

The term VOCs imply a range of chemical classes, including aliphatic, aromatic and chlorinated hydrocarbons; aldehydes; ketones; esters; ethers; acids; and alcohols. Many companies contribute directly or indirectly to environmental issues and concerns, but the nature and extent of their contributions depend on the chemical used. Existing guidance for Environment Agency Inspectors is given in a series of Process Guidance Notes. These divide VOCs into three categories:



However, the above three categories fail to encompass all types of VOCs. The Categorization of the unlisted VOCs depends on the judgement of the individual inspector of the environmental agencies.

A variety of methods or rules has been applied to categorize the unlisted VOCs and however, the vastness of the volatile compounds from both biogenic, anthropogenic sources resist to do so.

11.2.1 Sources of VOCs:

Through the use of a global model, it was found that natural emissions of non-methane hydrocarbons (NHMC) and VOCs exceed anthropogenic emissions. However, in urban areas, anthropogenic sources often dominate.

11.2.2 Natural Sources of Volatile Organic Compounds:

VOCs are present in a variety of natural sources, including trees, grasses, and even ocean waves. These types of VOCs can also be termed as biogenic volatile organic compound (BVOC).

BVOC (Biogenic volatile organic compound) is a chemical released into the air by plants. Biogeochemical cycling is the movement of chemicals between the biosphere and geosphere. The biosphere includes all living organisms. The geosphere consists of rocks, water, and soil. Soil is an important part of biogeochemical cycles in that it contains a large amount of organic matter which is broken down by microorganisms. This breakdown process releases carbon dioxide (CO_2) into the atmosphere as well as some volatile organic compounds (VOCs). VOCs are gases that easily convert biogenic volatile organic compounds (BVOCs) are a component of the natural atmosphere. In general, flowers and fruits emit the widest variety of BVOCs. These levels peak when the plants are mature.

Woody plants are more likely to release a diverse mixture of terpenoids, which includes isoprene, monoterpenes, sesquiterpenes and diterpenes. On the other hand, whereas grass like plants release comparatively huge quantities of oxygenated BVOCs along with little monoterpenes. When plants are damaged, the emissions of these compounds may be increased and other compounds may be released, which are known as green leaf volatiles which contains mainly long chain aldehydes and ketones etc. They include a variety of chemical compounds such as alcohols, acids, esters, and sulphur-containing gases. These substances play an important role in many ecosystems. BVOCs like terpenes, methyl jasmonate and methyl salicylate etc. are released from the tree leaves during abiotic as well as biotic stress on the woods. One might be familiar with BVOCs in their destructive forms: the stench from rotting vegetables or a skunk's spray are both unpleasant results of decomposition by microorganisms that produce BVOCs as metabolic by-products.

11.2.3 Why does plant synthesize BVOCs?

From the above discussion, it’s clear that a large number of volatile organic compounds are synthesized and emitted into the atmosphere by plants. Several research have confirmed that there exists an interconnection between biosphere and atmosphere which control the biosynthesis of BVOCs. Emission of particular type of volatile compounds as well as its rate of emission have been directly related to the alteration in the gene expression of the plants, microarray analysis of the leaves, alteration of enzyme activities etc.

Biosynthetic pathways of several BVOCs are not only limited to the physiological factors of the plants but also it depends on the physicochemical constrictions like temperature, atmospheric pressure over leaves, partial pressure.

Atmospheric effects like moisture availability in soil, concentration of greenhouse gases in the atmosphere, quantity of dust particles in the air, condition of ozone layer in the stratosphere etc. significantly influence the production and release of BVOCs from the plants. Flux density of sun light controls the rate of emissions of volatile compounds from leaves directly and indirectly.

11.2.4 Anthropogenic Sources of VOCs:

There are three main groups of anthropogenic VOCs. These include NHMCs, OVOCs and halogenated hydrocarbons. [e.g., Chlorofluorocarbons (CFCs); Hydro fluoro carbons (HFCs)].

a. In urban areas, vehicle emissions are the main contributors to ambient volatile organic compounds. Fumes coming from liquid fuels containing aromatic compounds are emitted to the air; most of these aromatic compounds are added to gasoline for antiknock purposes, such as lead replacement.

b. Climatic, soil and vegetation changes have been shown to affect the rates and pathways of C release from organic matter, but the role of oceans has received little attention. The major sources of marine organic carbon (OC) include planktonic and benthic production, as well as inorganic material and detritus from terrestrial sources.

Since the beginning of the industrial age, emissions of alkanes and alkenes have been dominated by anthropogenic sources, but also produced by soils, wetlands, and oceans.

c. Methanol, acetone etc. are the oxygenated hydrocarbons that are associated to vegetation, but also are emanated by combustion of fossil fuel. Methanol has a range of applications other than as a fuel additive. Acetone is used for industrial applications, as an antifreeze agent, an ingredient in nail polish remover, and a solvent in the paint industry.

These species play a role in both the global energy balance and climate change. The data set, which includes measurements from diverse locations around the globe, reveals that these two species can serve as useful tracers of the source of atmospheric CO, the most important greenhouse gas emitted by human activities.

d. Halogenated hydrocarbons are derivatives of hydrocarbon which include halogen (mainly fluorine and chlorine) in its structure. Toxic halogenated hydrocarbons include chloroform, a solvent; trichlorobenzene, used in the manufacture of dyes; PCBs and Dioxins, which are industrial by-products; hexachlorobutadiene, a major component of creosote and an unwanted ingredient in the manufacture of hydraulic fluid; and vinyl chloride, a precursor to PVC.

There are also a number of chemicals used as insecticides like DDT, lindane, aldrin etc. which contains halogenated hydrocarbons.

e. Methane is a greenhouse gas that is released in large amounts during the production of energy and as a result of human waste. It is also emitted by animals, particularly from cattle farms.

Summarily, it can be concluded that automobile emission and industrial waste are two major contributors to anthropogenic VOCs.

11.3 VOCs: What Role do they Play in Ecosystem?

11.3.1 Role of BVOCs:

a. Due to toxic, repellent, deterrent characteristics of some BVOCs released from flowers, leaves and roots can prevent or eliminate microorganisms. A new study shows that when maize roots are attacked by insects, a sesquiterpene compound is released.

b. In order to protect themselves from herbivores, plants have evolved a wide array of chemical defences. To defend themselves against these herbivores, plants use a variety of volatile organic compounds (VOCs). These VOCs can directly activate herbivore defence mechanisms or may prime a subset of defence-related genes for earlier and/or stronger induction on subsequent defence.

c. For flowering plants, creating seeds is essential for their survival. In order to achieve this, these plants release a multitude of BVOCs to attract the pollinators they need. An international team of researchers has found that exogenous application of isoprene promotes early flowering in barley (Hordeum vulgare) and oilseed rape (Brassica napus). Isoprene, a gaseous plant hormone, gives off the characteristic scent of pine trees.

d. BVOCs like isoprene and monoterpenes can shield the photosynthetic conduit of plants from impairment caused by momentary high-temperature episodes. These compounds accumulate in leaves during cool nights when the temperature is below optimum for photosynthesis. The next morning, when temperatures rise above optimum, some of these compounds are released. In plants, structural proteins are responsible for the formation of thylakoid membranes. Thylakoid membranes are made up of a system of stacked discs called thylakoids. These membranes have pores that allow the passage of molecules necessary for photosynthesis. When high heat is applied to them, they become leaky and lose their ability to produce energy efficiently. Isoprene that is released under stress from tree leaves strengthen the thylakoid membrane by increasing hydrophobic interactions between membrane proteins and lipids.

e. In biosphere, volatile organic compounds play an important role in the cycling of carbon and nitrogen, and thus are also involved in primary production. BVOCs quickly react with anthropogenic and natural compounds, as well as nitrogen oxides in the atmosphere. These reactions result in tropospheric ozone and photochemical smog. The dwelling time of greenhouse gases is increased due to the presence of BVOCs in the atmosphere. Consequently, secondary aerosols are formed in the atmosphere.

11.3.2 Role of VOCs from Anthropogenic Sources:

a. VOCs react with NOx in the presence of sunlight to form ground-level ozone, which is a component of smog. This substance can irritate your eyes, nose, throat and lungs. Smog is a serious problem in many metropolitan areas.

The presence of VOCs in the atmosphere has led countries to enact regulations to limit the total VOC emissions or to control specific VOCs that rise above a regulated threshold.

b. VOCs present in the air are an invisible killer. The soot and dust that are suspended in the air are only small particles of matter. The VOCs, on the other hand, are present in gaseous form and cannot be seen. They can cause serious damage to human health. One such gas is carbon monoxide. It is a poisonous gas that prevents blood from carrying oxygen to vital organs and tissues of the

c. There are many VOCs that can cause health problems, such as breathing disorders and cancer.

d. Volatile Organic Compounds (VOCs) are a major contributor to the urban heat island effect, which is when a city is significantly warmer than its surroundings.

11.4 Measurement of Quantity of VOCs in Air:

Measuring VOCs in air is a complicated task. The identification of VOCs in indoor/outdoor air requires specific methods, which are sensitive to low levels of VOCs and selective for the target compound. The method should be reliable and user friendly.

In order to determine the concentration of a specific volatile organic compound (VOC), you first need to know which VOCs are present. And that's not easy since there are many different VOCs and they're at low concentrations. Most VOC sensors are based on gas chromatograph (GC) technology, which is both expensive and time consuming. For example, GC-based sensors require a long warm-up time when turned on and produce an average measurement for the time period between turns on and off. Recently, researchers have tried to quantify the with required sensitivity by using sophisticated instruments like Gas Chromatography with Flame Ionisation Detector (GC-FID), Photo ionization detectors (PID), Proton Transfer Reaction-Mass Spectrometry (PTR-MS), High Performance Liquid Chromatography (HPLC) etc. The cryo-trapping method is very effective at trapping volatile organic compounds (VOCs) as most of the VOC boiling points are higher than the liquid nitrogen temperature (~77 K). However, handling of liquid nitrogen requires skilled person. Dry ice (solid CO_2) can be an alternative to liquid nitrogen for its easy handling procedure.

11.5 Preventive Measures to Control VOCs:

Air quality is one of the most important health indicators for both people and our planet. Air pollution is a complex issue that can be caused by many different factors. We have learned that VOCs play pivotal role in deciding the air quality.

The Air Quality Health Index (AQHI) is a great way to view air quality in our community and to understand how it can affect our health.

The AQHI measures the volume of pollutants in the air and provides a number that corresponds to how sensitive you are to those pollutant levels. It's based on standards set by the World Health Organization. Both the Government as well as person individual should take initiative to reduce the emission of VOCs.

Methods to lessen use and emissions of VOCs depend significantly on the specific process and product, but some methods include:

a. Tighten emission standards of motor vehicles and industries.

b. One should update and replace older heating units that run on propane or natural gas. While these fuels release fewer VOCs than oil, they still produce some harmful pollutants in the manufacturing process.

c. To control VOCs in indoor air emissions by choosing to purchase environmentally friendly cleaning products and supplies.

d. To store unused chemicals in a garage or shed. Chemicals should never be stored inside the house, where people spend much time.

e. To combat contaminated air (filled with VOCs), increase ventilation by opening doors and windows. Fans can be used to maximize air brought in from the outside which in turn will increase amount of fresh air in room.

f. To substitute commercially available paints with powder coating or UV-cured paint etc.

g. To use solvent-free or extremely low volatile solvents (ionic liquids, deep eutectic solvents, super critical CO2) to run chemical processes.

11.6 Conclusions:

Understanding how VOCs contribute to environmental pollution is important in order to create more sustainable cities for the growing urban populations. Cities are some of the most polluted places on Earth. In fact, one in eight deaths in cities is caused by air pollution. The problem is not limited to Asian and African megacities but is a global issue as more than half of the world’s population live in urban areas. Air pollution is often a by-product of vehicle traffic, which has increased with the growth of urban populations and the advent of industry.

Therefore, it is important for city planners to be more conscious about how they can create sustainable solutions for transportation needs, which will ultimately reduce the burden on public health and help create healthier environments for everyone. Aggressive research programme is quite necessary to find sustainable tools or methods like production of user-friendly products with high thermal stability and low vapor pressure to fight against growing VOCs in earth ecosystem.

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