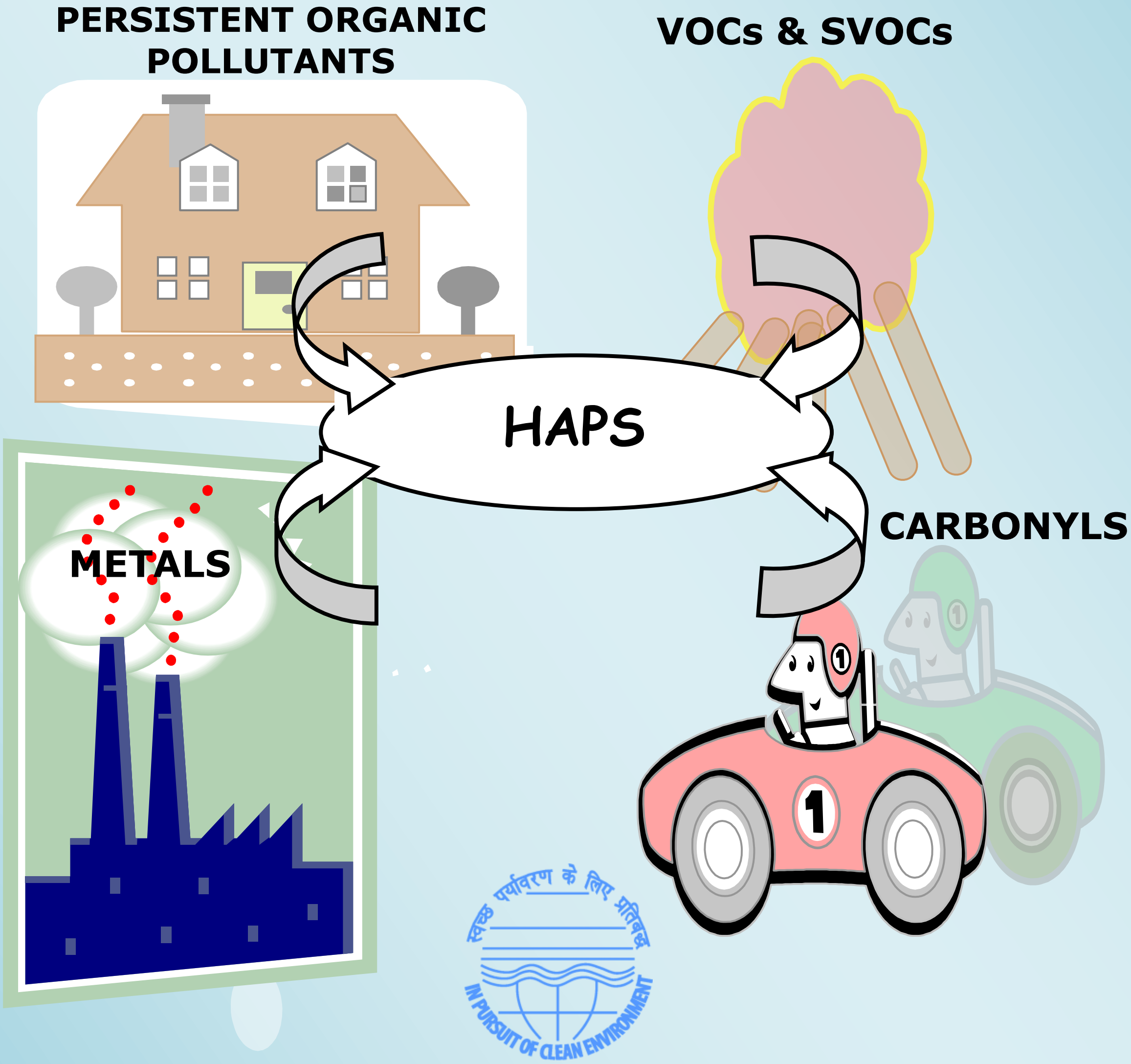
PARIVESH

HAZARDOUS AIR POLLUTANTS



CENTRAL POLLUTION CONTROL BOARD
MINISTRY OF ENVIRONMENT & FORESTS
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EDITORIAL

Air pollution got aggravated with the development and industrialization in the country. Growing cities, increasing traffic, the high influx of population to urban areas, increase in consumption patterns, higher levels of energy consumption, unplanned & rapid urban, industrial & economic development has led to a higher rate of increase of air pollution in urban areas. The burning of fuels for industrial activities and transportation leads to a plethora of combustion products, which contribute towards air pollution including toxic trace organics. Exposure to these toxic air pollutants can cause serious health effects, including damage to the immune system, respiratory, neurological, and reproductive and other health problems. Air toxics 'hazardous air pollutants' (HAPs) are present in the environment at low concentration (other than criteria pollutants) that are known, or suspected to be as toxic and persistent. Trace organics belong to the category of air toxics. Most air toxics originate from human made sources, including mobile sources (vehicles etc) and stationary sources like refineries, petrochemical industries, pharmaceuticals, dye & dye intermediate, paint & varnish, incineration, power plants, coke ovens, steel & other metallurgical plants besides indoor & non-point sources like pesticides & cleaning solvents. HAPs include volatile organic compounds such as benzene, toluene, polycyclic aromatic hydrocarbons like benzo(a)pyrene , persistent organic pollutants like PCBs, dioxins & furans and pesticides and heavy metals including arsenic, lead, mercury. This newsletter includes detailed information about possible sources, measurement techniques, ambient air levels & health hazards of these HAPs.

Because of initiatives taken for controlling air pollution from different sources, particularly automobiles and fuel quality, the increasing trend of toxic organic pollutants in Delhi has reduced. Polycyclic Aromatic Hydrocarbons content has been restricted to 10% in diesel to be supplied and Benzene content has been restricted to 1% in gasoline all over India from 2005. The initiative taken for improvement of fuel quality, introduction of compressed natural gas (CNG) and tightening of emission norms for vehicles have monitored unabated increase of pollution.

Efforts of Dr. S. K. Tyagi, Scientist 'C' for collecting and collating relevant information under guidance of Dr. S.D. Makhijani , Director, Dr. B. Sengupta, former Member Secretary and Shri J.S. Kamyotra, Member Secretary, CPCB are admirable for bringing out this newsletter.

The information will prove worthy to all concerned with protection and improvement of air quality.

(S.P.Gautam)

CHAIRMAN,
CENTRAL POLLUTION CONTROL BOARD

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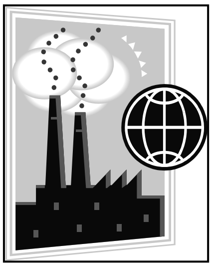
CHAPTER 1

INTRODUCTION



There has been a tremendous spurt in the use of petroleum products in highway, railway and marine transport. As an inevitable consequence, the combustion residues of gasoline and oil emerged as new factors in community air pollution. Examples of toxic air pollutants include benzene, which is found in gasoline; Perchloroethylene, which is emitted from some dry cleaning facilities; methylene chloride, which is used as a solvent and paint stripper by a number of industries; dioxins; asbestos; toluene; and metals such as cadmium, mercury, chromium, and lead. The contribution of automobile engine exhausts to the atmosphere is a potential hazard. The current economic trends and knowledge about the current lifestyle worldwide indicate that air pollution due to hydrocarbons, petrochemical products and engine exhausts will continue to increase in most of the metropolitan cities in the future.

Air pollution comes from many different sources such as factories, power plants, dry cleaners, cars, buses, trucks and even windblown dust and wildfires. It can threaten the health of human beings, trees, lakes, crops, and animals, as well as damage the ozone layer and buildings. Air pollution also can cause haze, reducing visibility.

The **WHO (1999**) has defined “Air pollutants” as ‘substances’ put into air by the activities of mankind, in such concentrations, which are sufficient to cause harmful effect to human health, vegetation, property or to interfere with the enjoyment of property.

Air pollutants change the composition of the atmosphere and affect the biotic environment. Some of the pollutants of concern are particulate matter (smoke, fumes etc); oxides of carbon, nitrogen and sulphur; hydrocarbons; metals; oxygenated compounds (alcohols, aldehydes, acids, etc.); ozone and other oxidants; etc. Two general groups of pollutants, based on their nature of formation, have been identified, viz. Primary pollutants and Secondary pollutants. Primary pollutants are those that are directly emitted from the source e.g., Sulphur dioxide (SO_2), Nitric oxide (NO), carbon monoxide (CO), etc. Secondary pollutants are those that are formed in the atmosphere as a result of reactions between normal air constituents and primary pollutants or amongst primary pollutants only, e.g., Sulphur trioxide (SO_3), Nitrogen dioxide (NO_2), peroxy acyl nitrate (PAN), etc. Another classification of pollutants depending on their nature defines two kinds of pollutants, viz. critical pollutants and hazardous air pollutants. Oxides of sulphur, oxides of nitrogen, carbon monoxide, Ozone and suspended particulate matter are some of the critical pollutants. Most of the pollutants, related to petroleum production, processing and use, have an intrinsic toxic potential which permits them to be included in **the 'Hazardous Pollutants'** category. Their photochemical reaction products are more dangerous than the original pollutants and may affect biological systems at extremely low concentrations.

The magnitude of harm caused by air pollutants depends on the dispersion levels, i.e., the extent of their transport from their original point of emission. Meteorological parameters like wind velocity, wind direction, turbulence and mass diffusion are the important and dominant mechanisms in air pollutant dispersal from stationary and mobile sources to downwind areas. The stronger the wind, the greater will be the dissipation and dilution of pollutants. In case of stack pollution, the degree of harm caused depends on the height at which the pollutants are being emitted. This is because the meteorological parameters at the emission point depict the direction taken by the pollutants (i.e. upwards, downwards, etc.).

Emission standards have been fixed to facilitate effective air pollution control. These standard permissible limits are formulated by the Central Pollution Control Board, Ministry of Environment & Forests; Bureau of Indian Standards (BIS) and the World Health Organisation (WHO). A large number of substances used in manufacturing and commerce have been recognized officially as hazards to industrial workers, and maximum limits of acceptable concentration for 8 hr. exposure have been established.

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CHAPTER 2

AIR POLLUTION IN URBAN AREAS

The higher incidences of respiratory diseases (like lung cancer) in urban areas can be ascribed to higher levels of pollutants in the city environments. Air pollution has been aggravated by developments that typically occur as countries become industrialised: growing cities, increasing traffic, rapid economic development and industrialisation, and higher levels of energy consumption. The high influx of population to urban areas, increase in consumption patterns and unplanned urban and industrial development has led to a higher rate of increase of air pollution in urban areas. The problem is aggravated by the inadequacy of pollution control measures, lack of proper enforcement of laws and regulations, increasing desertification, and decreasing vegetation cover. Currently, in India, air pollution is widespread in urban areas wherein **vehicles are the major contributors** and in a few other areas with a high concentration of industries and thermal power plants. **Vehicular emissions are of particular concern since these are ground level sources and thus have the maximum impact on the general population.** Also, vehicles contribute significantly to the total air pollution load in many urban areas.

An estimated 2000 metric tonnes of air pollutants are pumped into the atmosphere every day in Delhi. Vehicular sources contribute about 63% of the total pollutants, followed by industries and thermal power plants (29%) and the rest (8%) from the domestic sector. **(ISEST, 2000)**

A rapid increase in urban population; vehicular population; power generation and other harmful activities like diesel-based captive power generation units, waste burning and construction activities, have resulted in unplanned urban development, increase in consumption patterns and higher demands for transport, energy and other infrastructure, thereby leading to pollution problems. Between 1951 and 1991, the urban population has tripled, from 62.4 million to 217.6 million. The number of motor vehicles has increased from 0.3 million in 1951 to 37.2 million in 1997 **(MoST 2000)**, out of which 32% are concentrated in 23 metropolitan cities. Since 1950-51, the electricity generation capacity in India has multiplied 55 times from a meagre 1.7 thousand MW to 93.3 thousand MW **(MoEF 2000)**. The increased dependence of the power sector on coal has been associated with emissions from power plants in the form of particulate matter, toxic organic compounds, toxic elements, fly ash, oxides of nitrogen, sulphur and carbon besides ash, which require vast stretches of land for disposal.

Many of the toxic air pollutants, released in the urban environs, contribute to another harmful impact on the environment i.e., climate change. Research has proven that the global climate is warming up. According to IPCC's assessment, Methane is 20 times more potent than carbon dioxide as a greenhouse gas. Pollutants resulting from the use of the conventional energy sources (e.g. coal, petroleum) generally arise from a large number of points within a community, cause a general deterioration of the air over large areas.

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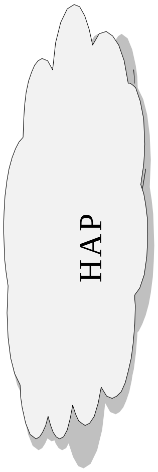
CHAPTER 3

HAZARDOUS AIR POLLUTANTS/AIR TOXICS



"HAZARD" is the set of inherent properties of a chemical substance or mixture which makes it capable of causing adverse effects on environment and man; when a particular degree of exposure occurs **(Richardson, 1986)**. Ambient air contains many compounds that are potentially hazardous to human health or the environment. Toxic air pollutants are also known as hazardous air pollutants (HAPs). While there is no universally accepted definition for air toxics, the more recognized definitions share a number of common elements. In general terms, "Hazardous air pollutants (HAPs) are defined as chemicals in the atmosphere that in sufficient concentration may have adverse effects on the health of humans and other animal species and may cause damage to ecological and social systems such as forests, agricultural crops and building materials **(Munn, 1995)**".

Most air toxics originate from human-made sources, including mobile sources (e.g. cars, trucks, buses) and stationary sources (e.g. refineries, petrochemical industries, power plants and steel plants) as well as indoor sources (e.g. some building materials and cleaning solvents). HAPs come from man-made and natural sources and include persistent organic pollutants, volatile organic compounds, polycyclic aromatic hydrocarbons, heavy metals **(Marrouf and Smith, 1998)**, etc.

Many organic compounds and some inorganic compounds may "volatilize" to some extent; this means that these compounds tend to evaporate at normal atmospheric temperatures and pressures when not contained. Common examples include the lighter components of gasoline such as benzene, which volatilize to a sufficient degree that they can be smelled (and sometimes seen) when cars are refueling at filling stations without vapor control systems.

These pollutants are suspected to cause cancer and other serious health effects, such as reproductive effects or birth defects, and adverse environmental effects. In 1970, HAPs were formally introduced into the United States Environmental Protection Agency (US EPA) Clean Air Act. It identifies HAPs as "pollutants which present or may present, through inhalation or other routes of exposure, a threat of adverse human health effects (including, but not limited to substances which are known to be, or may reasonably be anticipated to be, carcinogenic, mutagenic, teratogenic, chronically toxic) or adverse environmental effects whether through ambient concentrations, bioaccumulation, deposition, or otherwise as a result of emissions to the air.

It is estimated that about three million deaths occur globally each year due to air pollution, mainly by particulate matter (organic & inorganic). People exposed to toxic air pollutants at sufficient concentrations and durations may have an increased chance of getting cancer or experiencing other serious health effects. These health effects can include damage to the immune system, as well as neurological, reproductive (e.g., reduced fertility), developmental, acute and chronic respiratory illness, lung cancer, cardiovascular disease, mental health and stress-related disorders. Like humans, animals may experience health problems if exposed to sufficient quantities of air toxics over time. Besides these health effects, air toxics may also be a considerable nuisance, causing irritation of the eyes and mucous membranes and objectionable odour. Some persistent toxic air pollutants accumulate in body tissues and are further concentrated as they reach the next higher level in the food chain. As a result, man and other animals at the top of the food chain that eat contaminated fish or meat are exposed to concentrations that are much higher than the concentrations in the water, air, or soil.

Levels of methanic, nonmethanic and aromatic hydrocarbons in ambient air, as measured by CPCB, in Delhi during 2004 using continuous hydrocarbon analyzer are given in Table1 below. Total hydrocarbons are reported below 6ppm whereas NmHC were below 2 ppm only. Benzene levels are reported below 19μg/m^3 whereas Toluene was below 48μg/m^3 only. Higher values were reported during winter months.

Table1 - Monthly Average Levels Measured at Asiad Village(Siri Fort), Delhi, 2004

Parameter	**Feb.**	**Mar.**	**April**	**May**	**July**	**Aug.**	**Sept.**	**Oct.**	**Nov.**	**Dec.**
CH_4 (ppm)	3.44	4.0	4.2	3.3	1.9	1.8	1.8	2.2	2.3	2.1
NmHC (ppm)	0.93	1.8	1.1	1.8	1.2	0.9	0.9	1.2	1.6	1.2
THC (ppm)	4.36	5.8	5.3	5.2	3.0	2.7	2.7	3.3	3.9	3.3
Benzene (μg/m^3)	5.2	5.1	3.9	6.5	5.8	7.2	8.5	7.1	13.5	18.4
Toluene (μg/m^3)	9.6	10.3	7.7	13.2	10.0	9.7	13.0	18.6	35.9	47.3

Note: Hydrocarbon Analyser was out of order during Jan & June, hence could not be measured

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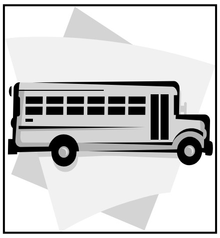
CHAPTER 4

SOURCES OF HAZARDOUS AIR POLLUTANTS

Human-made sources are the major sources for most of the air toxics, including mobile sources (e.g., cars, trucks, buses) and stationary sources (e.g., factories, refineries, power plants), as well as indoor sources (e.g., building materials and activities such as cleaning). Motor vehicles account for more air pollution than any other single human activity. More than half of the global emissions of carbon monoxide, hydrocarbons and nitrogen oxides from fossil fuel combustion derive from automobiles, both gasoline- and diesel-powered, and the proportions may be significantly higher in city centers. Transport-associated emissions affect the state of the environment by increasing air pollution levels, particularly carbon monoxide, volatile organic compounds, hydrocarbons, nitrogen oxides, ozone and lead, as well as dust and particles.

Mobile sources



Motor vehicles emit several pollutants that EPA classifies as known (e.g. Benzene) or probable human carcinogens (e.g. formaldehyde, acetaldehyde). Some toxic compounds are present in gasoline (e.g., Benzene) and are emitted to the air when gasoline evaporates or passes through the engine as unburned fuel. A significant amount of automotive benzene comes from the incomplete combustion of compounds in gasoline such as toluene and xylene that are chemically very similar to benzene. Like benzene itself, these compounds occur naturally in petroleum and become more concentrated when petroleum is refined to produce high octane gasoline. Formaldehyde, acetaldehyde, diesel particulate matter, and 1,3-butadiene are not present in fuel but are by-products of incomplete combustion. Formaldehyde and acetaldehyde are also formed through a secondary process when other mobile source pollutants undergo chemical reactions in the atmosphere.

Box 1 - Mobile Source Air Toxics

Acetaldehyde, Acrolein, Arsenic Compounds, Benzene, 1,3-Butadiene, Chromium Compounds, Dioxin/Furans, Diesel Particulate Matter + Diesel Exhaust Organic Gases (DPM + DEOG), Ethylbenzene, Formaldehyde, n–Hexane, Lead Compounds, Manganese Compounds, Mercury Compounds, MTBE, Naphthalene, Nickel Compounds, Polycyclic Organic Matter, Styrene, Toluene, Xylene.

Stationary sources

Sources can release vapors when handling highly-concentrated or pure organic compounds, as well as when solids and liquids with low levels of organic contamination are exposed to the atmosphere. Volatilization releases are common from chemical manufacturing and processing operations, from metal cleaning and dry cleaning operations that use organic solvents, and from waste management facilities.

Fig 1 - Burning of Hazardous wastes

Sources of methane (one of the GHGs) include natural sources like wetlands, gas hydrates in the ocean floor, permafrost, termites, oceans, freshwater bodies, and non-wetland soils. Fossil fuels, cattle, landfills and rice paddies are the main human-related sources. Previous studies have shown that new rice harvesting techniques can significantly reduce methane emissions and increase yields.

Table 2 - Annual Emissions of HCs due to different stationary activities (kg)

S.No.	Activity	Delhi	Mumbai	Kolkata	Chennai
1.	**Dry Cleaning**	1.3175E+06	1.1785E+06	1.1895E+06	7.7096E+05
2.	**Surface Coating**	1.8357E+07	2.7367E+07	2.2098E+07	1.0742E+07
3.	**Automobile Refinishing**	6.5037E+04	1.8876E+04	1.4137E+04	2.4601E+04
4.	**Toiletries**	1.4054E+06	2.0951E+06	8.2235E+05	1.2688E+06
5.	**Laundry Detergent**	4.3917E+04	6.5472E+04	2.5699E+04	3.9650E+04
6.	**Graphic Art Applications**	3.5814E+06	2.6189E+06	3.5420E+06	1.9135E+06
7.	**Newspaper Printing**	3.0604E+05	4.2814E+05	3.3838E+05	1.6123E+05
8.	**Petrol Loading**	1.3109E+06	9.3365E+05	3.6522E+05	4.2125E+05
9.	**Petrol Refueling**	4.0174E+06	2.7289E+06	1.1506E+06	1.2316E+06

Natural sources

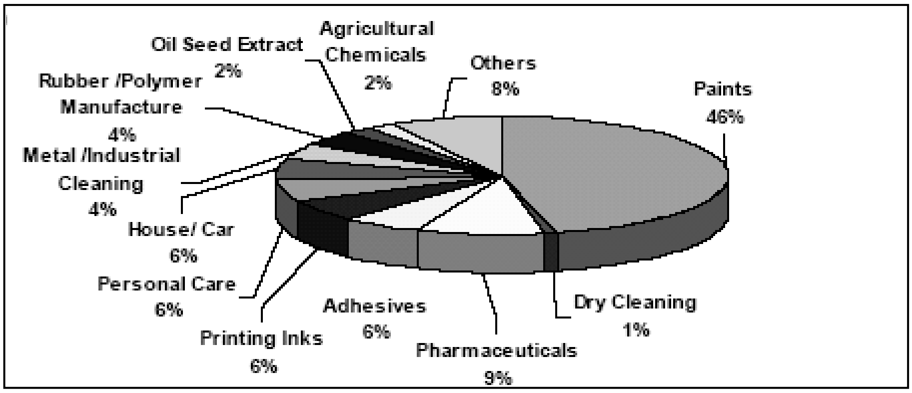
Volatilization is an important way by which some organic air pollutants are added to the atmosphere naturally. For example, in heavily forested areas, terpenes (volatile chemicals emitted from pines and other tree species) can account for a large proportion of total organic air pollution.

In addition to exposure from breathing air toxics, people are exposed to toxic air pollutants in many ways such as:

- Breathing contaminated air.
- Eating contaminated food products, such as fish from contaminated waters; meat, milk, or eggs from animals that fed on contaminated plants; fruits and vegetables grown in contaminated soil on which air toxics have been deposited.
- Drinking water contaminated by toxic air pollutants.
- Ingesting contaminated soil*.
- Touching (making skin contact with) contaminated soil, dust, or water (for example, during recreational use of contaminated water bodies).

*Some toxic air pollutants such as mercury can deposit onto soils or surface waters, where they are taken up by plants and ingested by animals and are eventually magnified up through the food chain.

Fig 2 - Percentage of Solvents Used in Different Sectors and Consumer Products



Box 2- Consumer Products Exposing Humans Are To Toxic Hydrocarbons

- ☞ Aerosol paint concentrates
- ☞ Automobile body polish and cleaners
- ☞ Drain pipe solvents
- ☞ Furniture polish and cleaners
- ☞ Household surface cleaners
- ☞ Insecticides for crawling & flying insects (aerosols)
- ☞ Laundry starch preparations
- ☞ Lubricating greases
- ☞ Leather dressings and finishes (e.g., shoe polish)
- ☞ Lubricating oils
- ☞ Non-Wood upholstered office side and arm chairs
- ☞ Personal Care Products (nail polish, nail polish remover, hairspray, hair color, and antiseptics)
- ☞ Inks & Adhesives
- ☞ Paint and varnish removers
- ☞ Waterproofing compounds

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CHAPTER 5

CLASSIFICATION OF HAZARDOUS AIR POLLUTANTS

The HAPs can be divided into four general categories, namely

1) Volatile Organic Compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs) - Benzene, Toluene, Xylene and PAH
2) Persistent Organic Pollutants – PCBs, Dioxins & Furans and Pesticides
3) Carbonyls – Aldehydes & ketones
4) Metals – Lead, Mercury, Arsenic, Cadmium, etc.

The US EPA currently lists 188 substances as hazardous air pollutants under the US Clean Air Act (1990). The HAPs are listed in **Table 3**.

Table 3 - List of Hazardous Air Pollutants

1,2-Dibromo-3-chloropropane	Styrene oxide	Ethylene thiourea
1,3-Butadiene	Methylene chloride (Dichloromethane)	Cadmium Compounds
1,3-Dichloropropene	**Toluene**	Dimethyl phthalate
1,4-Dichlorobenzene(p)	1,1,2,2-Tetrachloroethane	Formaldehyde
2,4-D, salts and esters	1,2-Propylenimine (2-Methyl aziridine)	2,4-Toluene diisocyanate
2-Acetylaminofluorene	Hydrogen sulfide	4-Nitrophenol
2-Chloroacetophenone	Phosgene	Triethylamine
3,3-Dichlorobenzidene	Tetrachloroethylene (Perchloroethylene)	Heptachlor
3,3-Dimethoxybenzidine	Ethyl chloride (Chloroethane)	1,2-Diphenylhydrazine
3,3'-Dimethyl benzidine	Ethylene dichloride (1,2-Dichloroethane)	1,2-Epoxybutane
4-Aminobiphenyl	Methoxychlor	Hexamethylphosphoramide
Acetaldehyde	Hexane	4,4¬-Methylenedianiline
Acetamide	Hydrazine	Naphthalene
Acetonitrile	Hydrochloric acid	Nitrobenzene
Acetophenone	Hydrogen fluoride (Hydrofluoric acid)	4-Nitrobiphenyl
Acrolein	Hydroquinone	Hexachlorobenzene
Acrylamide	Isophorone	Hexachlorobutadiene
Acrylic acid	Lindane (all isomers)	Hexachlorocyclopentadiene
Acrylonitrile	Maleic anhydride	Hexachloroethane
Allyl chloride	Methanol	Hexamethylene-1,6-diisocyanate
Aniline	Methyl bromide (Bromomethane)	Selenium Compounds
Asbestos	Methyl chloroform (1,1,1-Trichloroethane)	Manganese Compounds

Benzene (including benzene from gasoline)	Methyl ethyl ketone (2-Butanone)	Mercury Compounds
Benzidine	Methyl hydrazine	Fine mineral fibers3
Benzotrichloride	Methyl iodide (Iodomethane)	Nickel Compounds
Benzyl chloride	Methyl isobutyl ketone (Hexone)	**Polycyclic Organic Matter**
Biphenyl	Methyl isocyanate	Radionuclides (including radon)
Bis(2-ethylhexyl)phthalate (DEHP)	Methyl methacrylate	Arsenic Compounds (inorganic including arsine)
Bis(chloromethyl)ether	Methyl tert butyl ether	Antimony Compounds
Caprolactam	2-Nitropropane	Cobalt Compounds

Hazardous Air Pollutants are characterized as being vapors (not bound to particles, but existing as single molecules or very small aggregates "dissolved" in air – also called gaseous), particle-bound (reversibly absorbed or condensed onto the surface of particles), or particulate (irreversibly incorporated into airborne particles). Sources generally emit most metals (with the exception of mercury) as particles in the atmosphere.

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CHAPTER 6

METHODS OF MEASUREMENT

All sampling components leading to the organic analyzer shall be heated to a temperature >110°C (220°F) throughout the sampling period, unless safety reasons are cited. The essential components of the measurement system are described below:

- *Organic Concentration Analyzer* - A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120°C (250°F).

- *Sample Probe* - Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16 in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

- *Heated Sample Line* - Stainless steel or Teflon® tubing to transport the sample gas to the analyzer. The sample line should be heated (≥110°C) to prevent any condensation.

- *Particulate Filter* - An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

- *Recorder* - A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

- *Fuel* - A 40 percent H_2/ 60 percent N_2/ He gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

- *Zero Gas* - High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value*, whichever is greater.

- *Selection of Sampling Site* - The location of the sampling site is generally specified by the applicable regulation or purpose of the test (i.e., exhaust stack, inlet line, etc.).
- *Location of Sample Probe* - Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

- *Measurement System Preparation* - Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable.

- *Organic Measurement* - Begin sampling at the start of the test period, recording time and any required process information as appropriate.

*****Span Value means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit.

Method 25A, defined by the Environment Protection Agency for the determination of total gaseous organic concentration using a **flame ionization analyzer** is the most widely used method. The method measures total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, aromatic hydrocarbons. The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon. A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

Method 18, defined by the Environment Protection Agency for the measurement of gaseous organic compound emissions by **gas chromatography** is also a widely used method. The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles. The retention times of each separated component are then compared with those of known compounds under identical conditions. Therefore, the analyst can confirm the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst can then prepare or purchase commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst can also determine the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation. The gas chromatograph run time must be sufficient to clear all eluting peaks from the column before proceeding to the next run (in order to prevent sample carryover). Tubes filled with activated charcoal, with glass wool plugs at each end, are used to adsorb organic vapors, i.e., activated charcoal tubes are used for sample collection. The sampling flow is between 0 to 500ml per minute. A carrier gas (mostly Nitrogen), oxygen and fuel (mostly Hydrogen) are needed to run GC and detector. Gas Chromatograph column should be such that complete separation of desired components occurs and there exists an option for temperature programming. The GC should be calibrated before sample analysis.

Passive air samplers (PAS) are recently being employed for ambient air monitoring of POPs **(Lohmann et al., 2001; Shoeib et al., 2002)**. A PAS is a device that collects chemicals from the atmosphere without the help of a pump **(Muir et al., 1993; Kylin et al., 1994)**. Specifically semi permeable membrane devices and polymer coated fibers, glass disks, stir bars, and silicone tubing has been employed for this purpose. The primary advantage of passive sampling is its simplicity and low expense **(Ockenden et al., 1998; Ockenden et al., 1998; Khaled et al., 2000; Wilcockson et al., 2001; Wennrich et al., 2002)**. Responding to the growing need for inexpensive and simple monitoring of POPs, a PAS with XAD-2, a styrene-divinyl benzene copolymer as sampling medium has been developed. These are suitable for the measurements of long term average concentrations at the levels occurring at remote areas **(Wania et al., 2003)**.

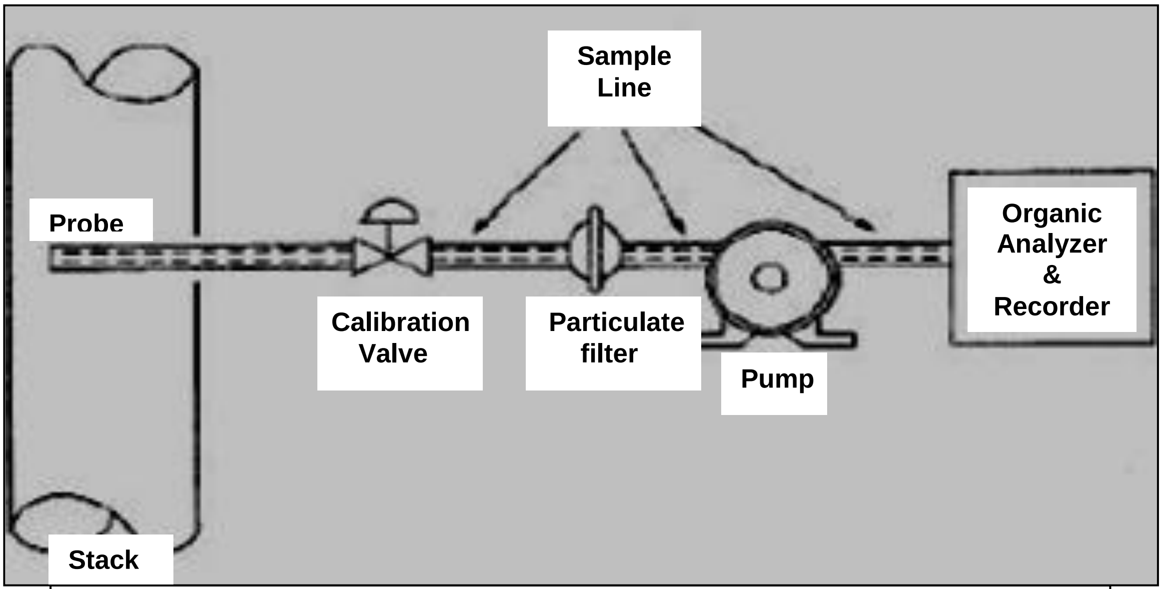
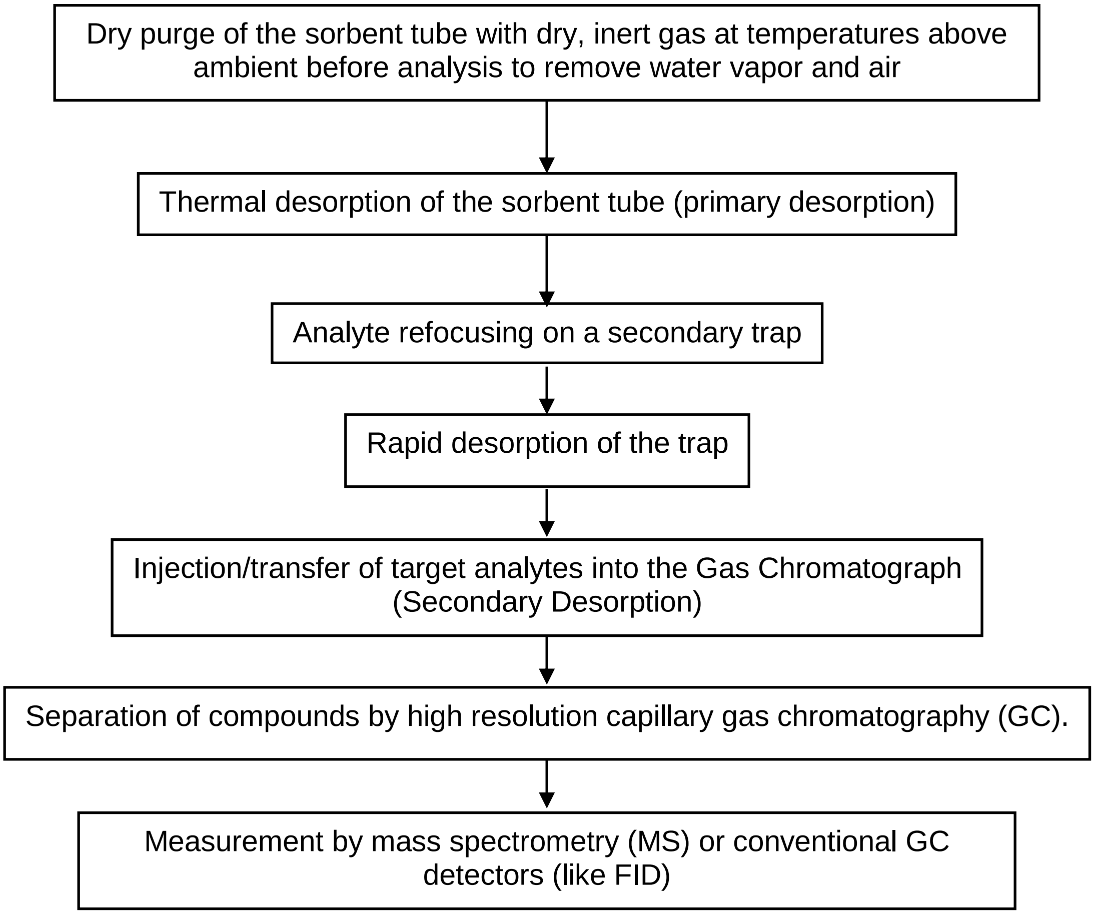


Fig 3 - Organic Concentration Measurement System

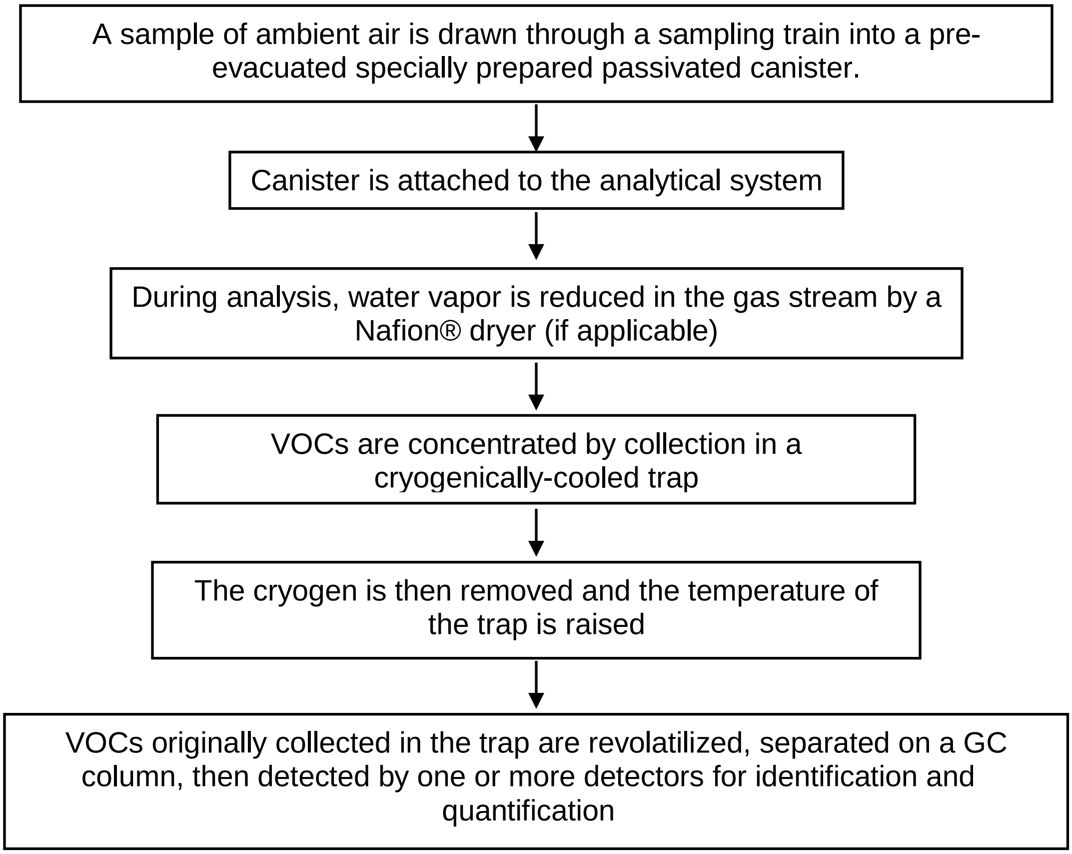
Method TO-17 is recommended by the Environment Protection Agency (EPA) for the determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Active Sampling onto Sorbent Tubes

Flowchart 1 – VOC METHOD TO-17



Method TO-14A is recommended by the EPA for the determination of Volatile Organic Compounds (VOCs) In Ambient Air using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography.

Flowchart 2 – VOC METHOD TO-14A


A sample of ambient air is drawn through a sampling train into a pre-evacuated specially prepared passivated canister.

Canister is attached to the analytical system

During analysis, water vapor is reduced in the gas stream by a Nafion® dryer (if applicable)

VOCs are concentrated by collection in a cryogenically-cooled trap

The cryogen is then removed and the temperature of the trap is raised

VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantification

The **Column** used in **GC** in TO 14A method is General OV-1 crosslinked methyl silicone (50-m x 0.31-mm I.D., 17 um film thickness), or equivalent; Carrier Gas Helium (~2.0 mL/min at 250°C); Injection Volume Constant (1-3 µL); Injection Mode Splitless; Initial Column Temperature -50°C; Initial Hold Time 2 min; Program 8°C/min to 150°C; Final Hold Time 15 min.

Mass Spectrometer-Mass Range 18 to 250 amu; Scan Time 1 sec/scan; EI Condition 70 eV

FID System - Hydrogen Flow ~30 mL/minute; Carrier Flow ~30 mL/minute; Burner Air ~400 mL/minute

Table 4 – Comparison of various non-specific detectors with a specific detector

Property	GC - FID/ ECD/ PID	GC - MS
Selectivity	Universal detector *(e.g., VOCs are within or not within permissible concentration range)*	specific detector
Extent of Error	More than GC-MS	-
Best Use	approximate quantification	Specific compound identification

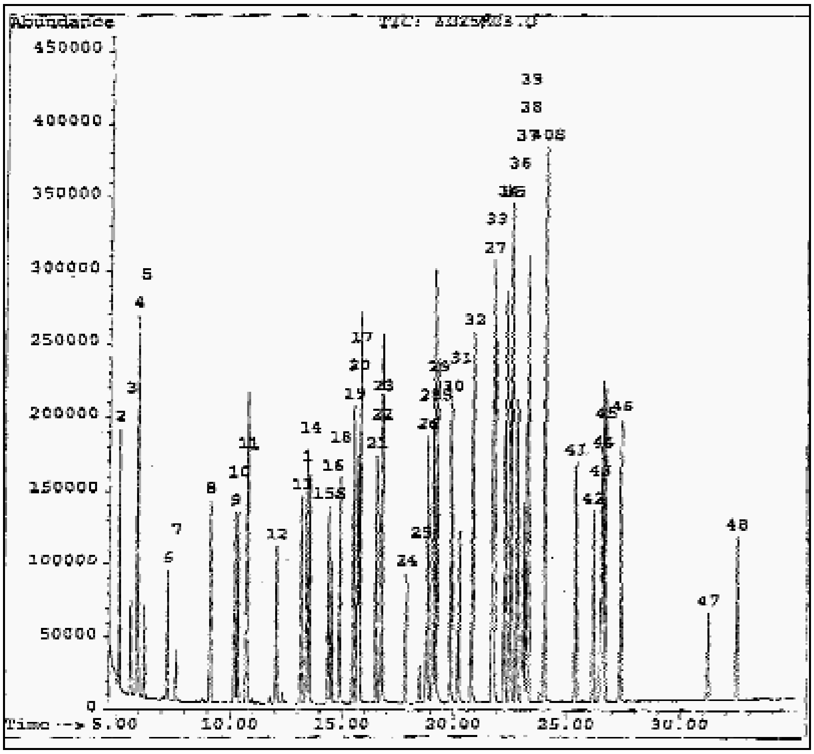
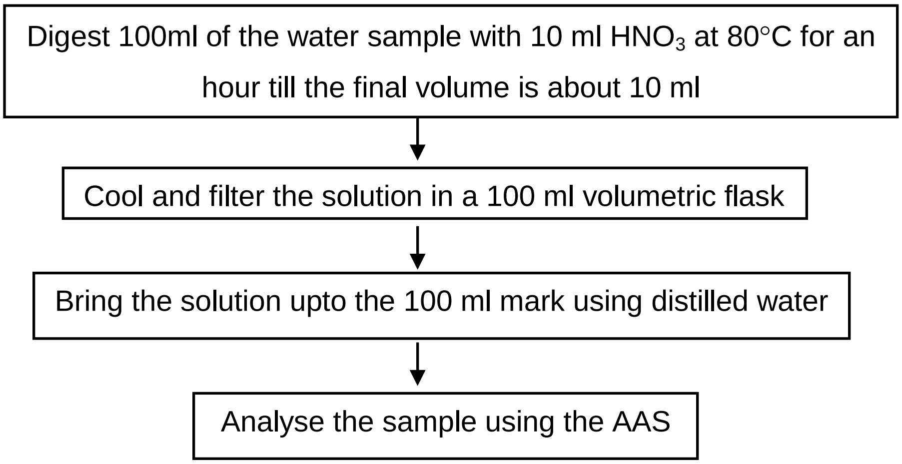


Fig 4 - A CG-MS generated choromatogram

Metals in the environment are usually measured with the help of Atomic Absorption Spectroscopy (AAS), but there are specific techniques for some critical pollutants like Mercury. Generally, the following procedure is used to quantify the metal conc. in soil and water.

Flowchart 3 - AAS Method for Metals



Digest 100ml of the water sample with 10 ml HNO_3 at 80°C for an hour till the final volume is about 10 ml

Cool and filter the solution in a 100 ml volumetric flask

Bring the solution upto the 100 ml mark using distilled water

Analyse the sample using the AAS

Digest 20 gm soil sample at 105°C for 24 hours till the final weight is about 1 gm. To 1 gm of soil, add 90 ml distilled water and 10 ml HNO_3.

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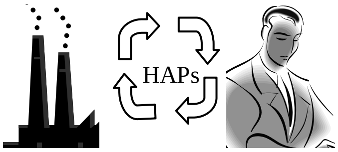
CHAPTER 7

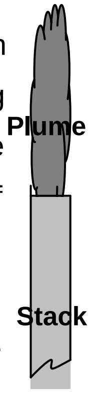
LIFE CYCLE ANALYSIS OF HAZARDOUS AIR POLLUTANTS



An understanding of how air toxics disperse and persist or are removed once released into the air is important information to aid in designing appropriate control measures. Several characteristics of the source (e.g., source height, gas exit temperature) can affect the movement of air toxics. Besides this, atmospheric and meteorological factors (particularly wind speed and direction) govern air toxics dispersion and transport. The fate of an air pollutant is governed both by transport processes and by the characteristics of the pollutant (e.g., its persistence, its ability to undergo reaction, tendency to accumulate in water or soil, or to concentrate in the food chain).

Three points need to be studied for analyzing the **life cycle of an air pollutant**, viz.-

- Where does a pollutant ultimately end up (e.g., air distant from the source, soil, water, fish tissue);
- How long it persists in the environment; and
- The chemical reactions which it undergoes.



The air space that the stack-emitted gaseous stream occupies, just above the stack, can be described as a plume. As the plume travels, it spreads and disperses, reducing ambient pollutant concentrations even though the cross-sectional mass of the plume remains the same. Eventually, the plume may intercept the ground. The combination of emission velocity, emission temperature (see below), vertical air movement and horizontal airflow all influence how high a plume will rise and how fast and far it will travel. The amount of pollutant mass at any given cross section in the plume is generally the same; thus, as the plume spreads, its concentration goes down. Stacks often push out gases by using fans resulting in providing a momentum to the emitted gases as the plume enters the atmosphere. **The combination of this momentum and the buoyancy of the stack gases (stack gases are warmer than the ambient air) cause the plume to rise.**

The combination of temperature and vertical velocity of stack emissions combine to affect the height to which the plume will rise and the layer of the atmosphere in which it will initially be transported. Besides temperature and velocity, there are some other factors which determine the overall ultimate effect of air pollutants on human and environment. These factors are listed in the table below. The ideal conditions, i.e., the desirable conditions so that the pollutant plume poses minimum hazard to man and environment can be created by keeping all these factors favourable.

The rate of dispersion of air pollutants is influenced by both the thermal structure of the atmosphere and mechanical agitation of the air as it moves over the different surface features of the earth. Once air toxics have equilibrated with ambient conditions (e.g., temperature, velocity), atmospheric and meteorological factors primarily influence dispersion and transport of air toxics. On windy days or when there is cloud cover such that there is neither strong heating nor cooling of the earth's surface, neutral stability occurs. **Neutral** conditions ("well mixed") neither encourage nor discourage air movement. Air lifted vertically will tend to remain at the higher level once the lifting force ceases. **An inversion is the worst condition** which can pose a huge health hazard by trapping the pollutants. Inversions occur whenever warm air over-runs cold air and "traps" the cold air beneath. Within these inversions there is little air motion, and the air becomes stagnant. If a nearby stack emits organic pollutants and they are transported to the ground layers due to unfavorable meteorological factors, an inversion can create havoc. High air toxic concentrations can occur within inversions due to the limited amount of mixing between the "trapped" air and the surrounding atmosphere.

Fate

Physical Processes For Removing Air Toxics

A number of important physical processes (processes that do not alter the chemical nature of pollutants) affect how air toxics move in and out of the atmosphere. In particular, this section discusses how gravity and precipitation remove air toxics from the atmosphere. The process through which particulates fall (or settle) to the surface in the absence of precipitation is known as dry deposition, and the removal of pollutants from the air through precipitation events is called wet deposition.

Dry Deposition - Dry deposition is the settling of particles due to gravity. The maximum speed at which a particle will fall in still air is known as the **settling velocity** (settling rate). A particle's settling velocity is a function of its size, density, and shape. Larger, denser particles settle more rapidly, and particles with more irregular shape settle more slowly. For particles smaller than a few microns in diameter (fine and ultra-fine particles), the gravitational settling rate is so slow that other forces, such as local air currents and collisions with gas molecules, tend to offset it. Thus, in the absence of other removal mechanisms (e.g., condensation and/or aggregation to form larger particles), particles in this size range tend to remain suspended in the air for long periods of time. Depending on the conditions, **fine particles may persist in the atmosphere for days or weeks** and travel hundreds or thousands of miles from their source. These particles pose a grave health concern as many of them fall in the respirable range, i.e., these can reach very deep in our respiratory system causing harm to the bronchi, bronchioles, alveoli and as deep as the alveoles.

At the other extreme, coarse dust particles (>50 microns in diameter), such as those generated while handling materials, have large settling velocities. Under normal conditions, such particles generated near the ground will deposit on the surface within a few seconds or minutes, generally within less than a kilometer of the source. Particles in between these two extremes in the size distribution will settle at intermediate velocities, and will distribute at intermediate distances from their sources.

Box 3 - Factors affecting air pollutant movement

Rate of release (exit velocity) - Large volumes of pollutants are often released at a relatively high velocity from stacks or vents, which can also serve to drive pollutants higher in the atmosphere, depending on the meteorological conditions.

Concentration (the mass of pollutant per unit volume of released gases) - Pollutants at higher concentrations may also be more likely to condense onto particles or liquid droplets.

Temperature - A plume that is warmer than the surrounding air will generally rise, which tends to increase the distance over which pollutants will be transported. Temperature of the plume also affects the physical form of pollutants which inturn affects the pollution level caused.

Height - Pollutants are released into the atmosphere at different heights. Greater release heights generally result in increased pollutant dilution in the atmosphere, lower ground-level concentrations, and a greater distance to peak ground-level concentrations. Release height also is important in evaluating local effects on air transport, such as building downwash.

Timing - The timing of release relative to specific meteorological conditions determines the particular dispersion and transport of pollutants.

Physical form - When sources release pollutants as particles (or if released gases condense into particles or adsorb onto the surface of existing particles), the rate of pollutant removal from the atmosphere to surfaces (e.g., plants, soils, surface water) depends upon particle size. As the size of particles increases, the rate at which particles fall due to gravity (settling velocity) increases. Bigger size particles (larger than about 20 microns in diameter) settle rapidly and may not transport far from sources of release. But, fine particles remain suspended in air indefinitely. Thus, the focus should be on removing the finer particles at the source itself.

Chemical form is generally more of a concern for inorganic pollutants, because organic chemicals tend to have well-defined chemical compositions and properties. For example, when Chromium is emitted in the hexavalent form (Cr^{6+}), it is highly reactive and is readily reduced under certain conditions to the trivalent form (Cr^{3+}) which is much less toxic to humans and animals than Cr^{6+}.

Wet Deposition - Wet deposition involves the “washing out” of pollutants from the atmosphere through precipitation events (including rain, snow, and in some cases hail). Wet deposition affects both particulate and vapor-phase pollutants. For larger particles and vapor phase pollutants that are soluble in water, precipitation is very efficient at removing pollutants from the air and depositing them on the earth’s surface. Wet deposition may be less efficient at removing fine particulates, and has limited effect on the levels of gaseous pollutants with high Henry’s Law constants (indicating low solubility in water compared to vapor pressure). Because wet deposition depends on the occurrence of precipitation events, it is best characterized over long periods (e.g., seasons or years). The relative importance of precipitation in removing pollutants from the air depends on the climatic conditions in the areas affected by pollution.

Chemical Reactions that Remove Air Toxics

In addition to deposition, chemical reactions may occur that reduce air toxics concentrations. Air toxics may be destroyed through the action of sunlight, through reactions with atmospheric chemical pollutants, or through a combination of these pathways. In estimating the ambient air concentration associated with air toxics’ releases, it is necessary to consider chemical reactions as well as the physical removal processes. All chemical reactions do not result in the destruction of air toxics, or their conversion to less harmful products but potentially more harmful pollutants may also be formed as a result of these chemical reactions (e.g., formation of secondary air pollutants like PAN – refer to Box no. 4).

Generally, organic compounds are much more susceptible to chemical reactions in the atmosphere than metals or other inorganic contaminants. The major chemical reactions undergone by organic chemicals in the atmosphere include:

- Photolysis (destruction by sunlight alone);
- Reaction with the hydroxyl radical ($OH^\bullet$);
- Reaction with the nitrate radical ($NO_3^\bullet$); and
- Reaction with ozone (O_3).

Often these reactions occur in combination with reactions that are strongly affected by sunlight. While reaction rates vary widely for pollutants, under typical atmospheric conditions, **reactions with the hydroxyl radical are the most rapid, and account for a large portion of pollutant degradation during daylight hours**. Reactions with nitrate radical occur primarily during the night, and reactions with ozone occur both day and night. Except in the case of a few pollutants, “pure” photolysis is a relatively minor reaction process. Other reactive species such as the hydroperoxide radical ($OOH^\bullet$) may also participate in pollutant degradation under some conditions. The relative importance of these reactions is dependent not only on climatic factors (e.g., duration and intensity of sunlight), but also on the overall concentration of pollutants. For example, high levels of the oxides of nitrogen (NOx) emissions and emissions of VOCs increase the levels of nitrate radicals and ozone in the atmosphere, thereby increasing reaction rates for subsequent reactions where these species are involved.

Examples of large-scale chemical reactions that result in products that can be hazardous to health include the formation of ozone and photochemical oxidant in areas with high levels of NOx and volatile organic emissions. In addition, there are many reactions of specific organic pollutants that generate air toxics of concern, as Table No. 16 shows. The importance of these reactions at any given location depends on the emissions and resulting concentrations of the precursor materials. In addition, many of these reactions are catalyzed directly and indirectly by sunlight, so weather and climatic factors are important in judging the importance of secondary reactions. While it is difficult to generalize, the secondary formation of formaldehyde and acrolein are thought to be important in many regions of the country with significant industrial and mobile source emissions.

Box 4 - Formation of Secondary Air Pollutants

Hydrocarbons are mainly involved in photochemical reactions in the atmosphere and result in the formation of a variety of toxic secondary pollutants. The presence of some secondary pollutants in the atmosphere results in a condition called the photochemical smog.

Smog arises from photochemical reactions in the lower atmosphere by the interaction of Hydrocarbons and NO_x released by exhausts of automobiles and some stationary sources. This interaction results in a series of complex reactions producing secondary pollutants such as Ozone, aldehydes, ketones and peroxyacyl nitrates. The conditions for the formation of photochemical smog are stagnation, abundant sunlight and high concentrations of Hydrocarbons and NO_x in the atmosphere.

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

$O + O_2 \longrightarrow O_3 + M$

$O_3 + NO \longrightarrow NO_2 + O_2$

$\text{hydrocarbon} + O \longrightarrow RCO^{\bullet}$

$RCO^{\bullet} + O_2 \longrightarrow RCO_3^{\bullet}$

$RCO^{\bullet}_3 + \text{hydrocarbon} \longrightarrow RCHO\ \text{(aldehydes) and}$
$R_2CO\ \text{(Ketones)}$

$RCO^{\bullet}_3 + NO \longrightarrow RCO^{\bullet}_2 + NO_2$

$RCO^{\bullet}_2 + NO \longrightarrow RCO + NO_2$

$RCO^{\bullet}_3 + NO_2 \longrightarrow RCO_3NO_2\ \text{(PANs)}$

$O_3 + \text{hydrocarbon} \longrightarrow RCO^{\bullet}_2 + RCHO, R_2CO$

The characteristic symptoms of such smog are brown haze in the atmosphere, reduced visibility, eye irritation, respiratory distress and plant damage.

Here are a few examples of Secondary Pollutants formed by reaction of primary organic pollutants with normal air constituents and other primary pollutants.

Table 5 – Secondary organic Pollutants

Pollutant	Formed From
Acetaldehyde	Propene, 2-Butene
Acrolein	1,3-Butadiene
Carbonyl Sulfide	Carbon Disulfide
O-Cresol	Toluene
Formaldehyde	Ethene, Propene
Hydrogen Chloride	Nitric Acid, Chlorinated Organics
Methylethyl Ketone	Butane, Branched Alkenes
N–Nitroso-N–Methylurea	N–Methylurea
N–Nitrosodiethylamine	Dimethylamine
N–Nitrosomorpholine	Morpholine
Phosgene	Chlorinated Solvents
Propionaldehyde	1-Butene

The overall lifetime ($1/r_{overall}$) of a chemical in the environment is equal to the sum of the atmospheric lifetime when considering only physical processes ($1/r_{physical}$) plus the lifetime when considering only chemical processes ($1/r_{chemical}$). This equation is the same as saying that the overall rate constant for pollutant removal/destruction ($r_{overall}$) is equal to the sum of the rate constant for physical removal ($r_{physical}$) plus the rate constant for chemical reaction ($r_{chemical}$). This relationship follows from the nature of first-order reaction kinetics, and is known to be only an approximate description of actual physical processes. It is a useful approximation, however, that can be used to evaluate the importance of atmospheric processes for many pollutants. **For any given air toxic, overall persistence in the atmosphere depends on particle-vapor partitioning behavior, particle size distribution (if the material is non-volatile), and susceptibility to various types of chemical reactions.** Atmospheric half-lives due to deposition (wet and dry) tend to be highly variable depending on particle size, ranging from a few minutes for coarse particles to many days for very fine particles. Most fine particles (less than a few microns) are removed from the troposphere (the lower level of the atmosphere where most weather takes place) with an average lifetime of between 5 and 15 days.

Table 6 - Rate Constant of Various Atmospheric Reactions of HAPs

Compound	r_{OH}	r_{O3}	r_{NO3}	$r_{photolysis}$
Methane	28,000	$2x10^8$	$2x10^6$	–
Ethane	8,40	$3x10^7$	$1x10^5$	–
Benzene	180	$4x10^6$	$4x10^6$	–
Toluene	37	$3x10^5$	$3x10^5$	–
1-Butene	7.4	26	93	–
Isoprene	2.3	20	1.4	–
Formaldehyde	19	–	–	5.5
Acetaldehyde	12	5,600	–	2.7

Where r_{OH} is the rate constant of a reaction with the Hydroxide radical

r_{O3} is the rate constant of a reaction with Ozone

r_{NO3} is the rate constant of a reaction with Nitrate ion

$r_{photolysis}$ is the rate constant of the photolysis reaction of a particular pollutant

Source: California Air Resources Board Toxic Air Contaminant Fact Sheets

Transport and Deposition of Mercury

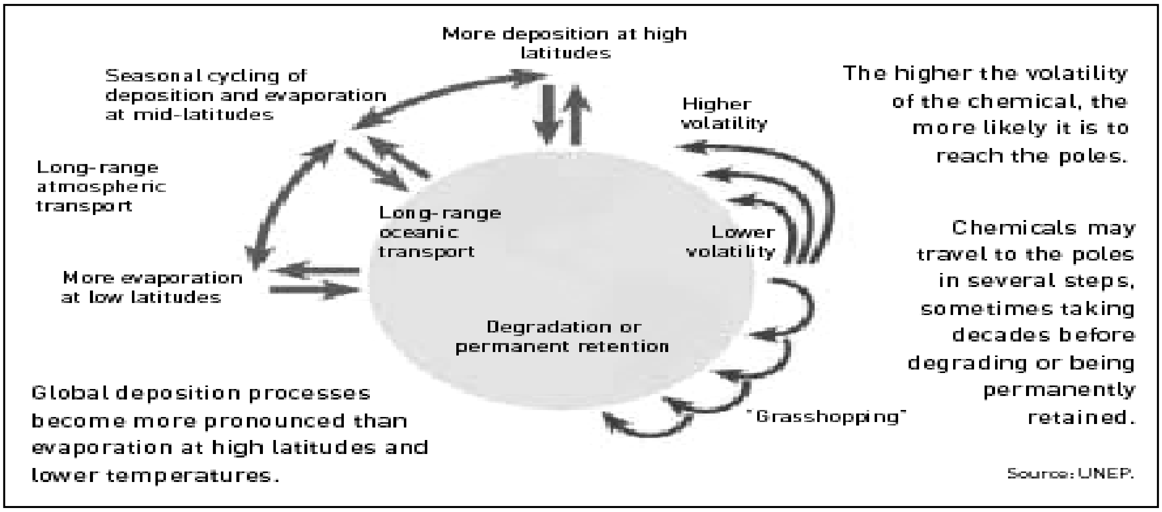


Fig 5 -Behaviour of Pollutants accross the Globe

Elemental mercury gas is nearly insoluble in water and rather inert chemically, so it can be transported up to thousands of miles while gradually being converted to other forms and deposited. The ionic form, Hg(II) or Hg^{2+}, is soluble in water and thus incorporated into rain, fog, and snow. Also, Hg(II) is both physically and chemically active and is known as “reactive gaseous mercury” or RGM. Most of the Hg(II) emitted is deposited via both precipitation and dry gases within about 30 to 60 miles from the stack/source. In many cases, this “local” deposition can be the most important impact of mercury from combustion sources. The fate of particle-bound mercury depends on the size of the particles, though generally they deposit on earth within a few hundred miles of the emitting stack.

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CHAPTER 8

STANDARDS PERMISSIBLE LIMITS OF HAPs

S.No.	Compound	Max. Permissible Conc. (mg/m^3)			
		Australia	USA	UK	Germany
1.	Acrylonitrile	45	4.5	4.0	50
2.	Benzene	-	0.016	0.005	-
3.	Methylene chloride	720	360	700	500
4.	Propylene oxide	240	50	50	-
5.	Phenol	19	19	-	-
6.	Formaldehyde	1.5	1.2	2.5	0.6
7.	Parathion	-	0.1	0.1	0.1
8.	Heptachlor	-	0.5	0.5	0.5
9.	Dichlorvos	-	1	1	1
10.	Acetaldehyde	180	180	180	90
11.	Hexachlorobenzene	-	0.25	-	-
12.	Vinyl chloride	-	2.6	18.2	18.2
13.	PAH	-	0.001	-	-
14.	Carbon tetrachloride	30	63	65	20
15.	Carbaryl	-	5	5	5
16.	Acrolein	0.25	0.25	-	0.25
17.	Acrylamide	0.3	0.3	0.3	
18.	n-Hexane	360	176	360	180
19.	Poly chlorinated biphenyls	-	0.5	0.5	-
20.	Ethylene oxide	90	2	10	
21.	Chloroform	50	50	50	50
22.	Tetra- chloroethylene	670	335	678	300
23.	Methyl isobutyl ketone	205	205	205	400
24.	Dimethyl formaldehyde	-	30	30	-
25.	Dioxins	-	0.000013	-	-

**** Ref:** WHO – IPCS (Health & Safety Guide for Occupational Exposure Limit Values)
The permissible levels cited above are 1980 onwards and are being continually revised.

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CHAPTER 9

VOCs & SVOCs

The organic compounds that evaporate easily are recognized together as volatile organic compounds. Technically such compounds are defined as organic compounds with a vapour pressure of 1300 Pascal (about 1% atmospheric pressure at sea level). These compounds may include several aromatic hydrocarbons and considered into the common category due to their similar physical behaviour in the atmosphere. These compounds have a boiling point range with lower limit between 50°C and 100°C and an upper limit between 240°C and 260°C where the higher refer to polar compound.

Table 7 - List of 62 VOCs (as per EPA Standard Method TO 15/17)

Acetone	Ethyl dibromide (1,1-Dibromoethane)	Ethanol
Benzene	4-Ethyltoluene	Ethyl acetate
Benzyl chloride	Trichlorofluoromethane (Freon 11)	Ethyl benzene
Bromoform	Dichlorodifluoromethane(Freon 12)	1,4-Dioxane
Bromomethane	1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)	Propylene
Bromodichloromethane	1,2-Dichlorotetrafluoroethane (Freon 114)	Styrene
1,3-Butadiene	Hexachloro-1,3-butadiene	Carbon disulfide
2-Butanone (MEK)	2-Hexanone (MBK)	Carbon tetrachloride
Dibromochloromethane	4-Methyl-2-pentanone (MIBK)	Chlorobenzene
1,2-Dichlorobenzene	Methylene chloride	Chlorethane
1,3-Dichlorobenzene	Methyl-tert-butylether (MTBE)	Chloroform
1,4-Dichlorobenzene	2-Propanol	Cyclohexane
1,1-Dichloroethane	1,1,2,2-Tetrachloroethane	Chloromethane
1,2-Dichloroethane	Tetrachloroethene	Heptane
1,1-Dichloroethene	Tetrahydrofuran	Toluene
cis-1,2-Dichloroethene	1,1,1-Trichloroethane	o-Xylene
trans-1,2-Dichloroethene	1,1,2-Trichloroethane	m-Xylene
1,2-Dichloropropane	Trichloroethene	p-Xylene
cis-1,3-Dichloropropene	1,2,4-Trichlorobenzene	Vinyl acetate
trans-1,3-Dichloropropene	1,2,4-Trimethylbenzene	Vinyl chloride
Hexane	1,3,5-Trimethylbenzene	

There are 15 high priority; 17 medium priority; and 20 low priority VOCs for India, as identified by the CPCB. The **15 high priority** ones are listed in the table below.

Box 5 - Priority Volatile Compounds

1. 1,3 Butadiene
2. Toluene
3. Vinyl Chloride
4. Acrylonitrile
5. Maleic anhydride
6. Toluedine Isocyanate
7. Epichloro hydrine
8. Phosgene
9. Benzene
10. Ethylene oxide
11. Propylene oxide
12. Caprolactum
13. Phthalic anhydride
14. Carbon tetrachloride
15. Hydrogen cyanide

VOCs emerge as evaporative emissions during handling, storage and use and as part of unburnt or partially burnt hydrocarbons mostly along with exhaust gases from vehicles. There are thousands of different VOCs produced and used in our daily lives.

Emission sources

Paints, Varnishes, Moth balls, Solvents, Gasoline, Newspaper, Upholstery, Fabrics, Cooking, Cleaning, Chemicals, Vinyl floors, Carpets, Photocopying, Sealing, Adhesives, Caulks, Cosmetics, Air Fresheners, Fuel Oil, Environmental Tobacco Smoke etc.

Health effects

Acute - Eye irritation / watering, Nose irritation, Throat irritation, Headache, Nausea/Vomiting, Dizziness, Asthma exacerbation

Chronic – Cancer, Liver damage, Kidney damage, Central Nervous System damage

The most commonly occuring chemicals of this class are BENZENE, TOLUENE and XYLENE (BTX). The BTX compounds are harmful toxic pollutants causing exposure related health effects in human beings. This group of VOCs is evidently carcinogenic in human beings. Due to the health aspects of BTX compounds, it is becoming extremely important to screen their presence and to determine prevailing concentration in the ambient environment.

a. Benzene, Toluene & Xylene

Sources

a) Transport: vehicular exhaust, fuel filling station, fuel adulteration, Railways, Airways.

b) Industries : Major industrial units -Refinery, petrochemical etc, industrial estates, Medium scale chemical industries

c) Domestic Emissions - Domestic combustion unit, Commercial combustion units.

Table 8 - Physico-chemical properties of Benzene, Toluene, Xylene

Properties	Benzene	Toluene	o-Xylene	m-Xylene	p-Xylene
Physical form (20ºC)	Clear colourless liquid	Clear colourless liquid	Colourless liquid	Colourless liquid	Colourless liquid
Flash Point (0ºC)	-11.1ºC	4.4ºC	30ºC	25ºC	25ºC
Flammable limits	1.3-7.1%	1.17-7.1%			
Melting/Freezing point	5.5ºC	-95ºC	-25.2ºC	-47.9ºC	13.3ºC
Boiling Point (760mm of Hg)	80.1ºC	110.6ºC	144.4ºC	139.1ºC	138.3ºC
Density (g/ml) (20ºC)	0.878	0.8669	0.876	0.860	0.857
Vapour pressure (26ºC)	**13.3 kPa**	**28.7mmHg**	**0.66**	**0.79**	**0.86**
Solubilities	Water: 1800 mg/lt at 25ºC; Non aq. Solvents: miscible with most	Fresh water: 535mg/lt at 25ºC Sea water: 380mg/lt at 25ºC	Water: 142 mg/lt	Water: 156 mg/lt	Water: 185 mg/lt

Toxicological and carcinogenic effects

Long term exposure to *benzene* causes Leukaemia in human beings. In animal studies, leukemia, lymphomas and other types of tumors are observed. Exposure to benzene is linked to genetic changes, increased proliferation of bone marrow cells and occurrence of certain chromosomal aberrations in humans and animals. USEPA has classified Benzene as Group A human carcinogen. In addition a number of non-cancer effects are associated with Benzene exposure such as disorders of blood, harmful effects of bone marrow, anaemia and reduced abilities of blood to clot, damage to immune system and acts as a reproductive and developmental toxicant. WHO estimates a 4 in 1 million risk of leukaemia on exposure to benzene to a concentration of 1µg/m^3 (0.31ppb). High levels of benzene exposure produce haematotoxic effects like leucopenia, lymphopenia and anaemia; neurotoxic symptoms; ventricular tachycardia and respiratory failure.

Toluene in comparison to benzene is less toxic and may cause drowsiness, impaired coordination etc. High dose exposure of toluene can produce kidney and liver damage and hyperplasia of bone marrow, anaemia, and depression in central nervous system which may lead to impairment of coordination and slowed reaction time.

Acute *Xylene* exposure may be marked by dizziness, weakness, headache, nausea, vomiting, breathing difficulty and loss of coordination. In severe exposure, there is visual blurring, tremors, heart beat irregularities, paralysis and loss of consciousness.

Table 9 - Quantification Techniques for BTX

Sampling	**ASTM**	**APHA**	**USEPA**	**EU**	**CPCB***
Method A			TO-14		
Device	Tubes with pumps	Tubes with pumps	Tedlar bags/ canisters	Tubes with pumps	Glass Tubes with low flow pumps
Medium	Charcoal	Charcoal		charcoal	Activated Charcoal (coconut shell, 60-80 mesh size)
Flow rate	100-200 mL/min	50-200 cm^3/min	100-200 mL/min		
Duration		1-3 hrs			2-4 hrs
Analysis					CS_2 Desorption , Capillary GC-FID
Method B			TO-17		
Device			glass tubes		Stainless Steel tubes with low flow pumps
Medium			Charcoal		Tenax
Flow rate			10-200mL/min		
Analysis	GC-FID	GC-FID	GC-FID,GC-MS	GC-FID	Automated Thermal Desorption - Capillary GC-FID
Detection limit		25 ppb (10 L air sampled)	≤ 0.5ppb		≤ 0.5ppb

*****Ref: Tyagi,2005; Kumar and Tyagi, 2006.

The average concentration of Benzene, Toluene and Xylene in the ambient air in various cities, as measured by different scientists, is represented in Table10.

Table 10 - Levels of BTX in different cities of the world

City	**Delhi**	**Ulsan (Korea**	**Asan (Korea)**	**Seoul (Korea)**	**New Jersey**	**Changchun (China)**	**Guangzhou (China)**	**Brimingham (UK)**	**North Calorina**	**Texas**	**Baltimore**
Duration	2001-02	June'97	August'01	August'01	Nov'92	July – Sep'98	May 2001	Mar'99-Feb'00	Aug-Oct'01	Apr-Nov'99	June 2001
No.of samples	11	10	30	30	11-35	450	40	473 (daytime), 99 (night time)	50	129 (canisters) 142(OVM)	420 (for 14 sites)
Benzene (µg/m^3)	2.3-15.5	2.1± 0.8	23.83	34.58	0.60-2.82	9.4-43.8	7.6-3.6	10.6	4.0	1.17	13.3
Toluene (µg/m^3)	5.1-27.5	3.9± 0.9	13.90	46.41	2.95-19.84	36.2-81.1	38.0 - 108.5	28.9	10.4	3.32	17.9
Xylene (µg/m^3)	1.1-15.9	2.7±1.7	8.28 (o-Xylene), 8.48 (p-Xylene)	9.29 (o-Xylene), 8.69 (p-Xylene)	0.32-3.87	12.1-23.4	4.6-26 (m,p-Xylene), 4.7-17.2 (o-Xylene)	7.6,2.7,3.1 for p,m,o, xylene resp.	4.5	0.78 (o-xylene), 2.00 (m,p-xylene	10.6 (m,p-Xylene), 3.65 (o-Xylene)
Reference	Tyagi, 2002	Kwangsm et al, 2001	Busson et al, 2003		David et al, 1996	Chunming et al, 2000	Chan et al, 2003	Young et al, 2002	Reideke et al, 2003	Pratt et al, 2005	Sapkota et al, 2005

Measurement Methodof BTX (German Dragger, BIS & CPCB Method)

The Central Pollution Control Board is monitoring the levels of BTX in the air using the following method.

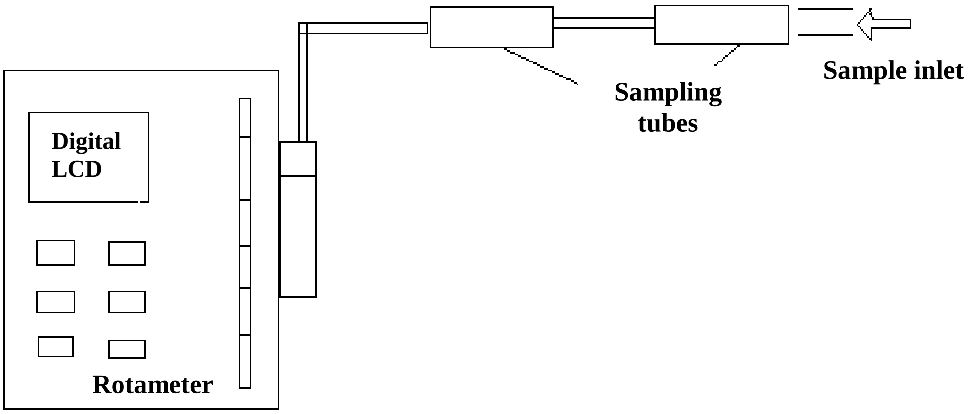
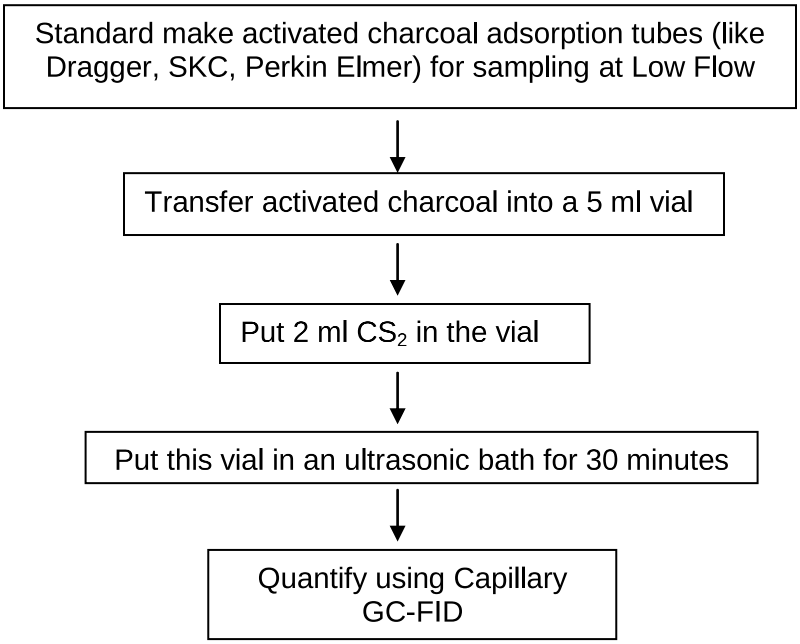


Fig 6 - Fig 6 - Active Sampling of Benzene, Toluene and Xylene from Ambient Method


Standard make activated charcoal adsorption tubes (like Dragger, SKC, Perkin Elmer) for sampling at Low Flow

Transfer activated charcoal into a 5 ml vial

Put 2 ml CS_2 in the vial

Put this vial in an ultrasonic bath for 30 minutes

Quantify using Capillary GC-FID

Flow Chart 5 - BTX Analysis using the Automated Thermal Desorption GC-FID Method

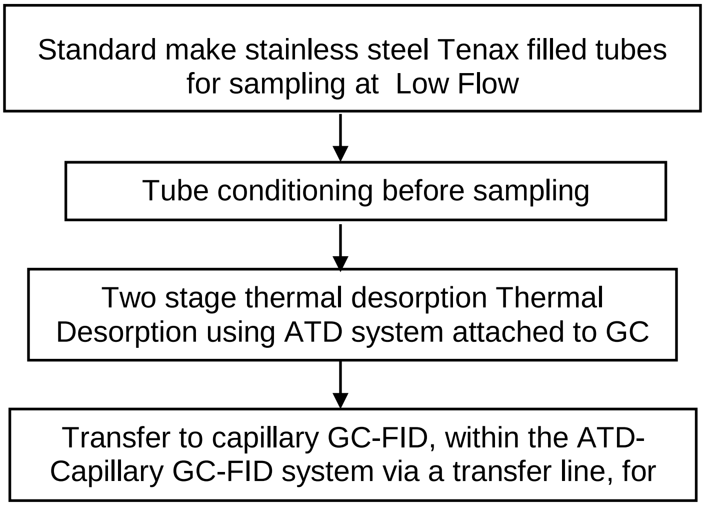


Table 11 - Air Quality Standards for Benzene in different Countries

Country	Standard Concentration	To be achieved by
UK	16 µg/m^3 – running annual mean	31st Dec., 2003
European Commission	5 µg/m^3 – annual average	31st Dec., 2010
Japan	3 µg/m^3 - annual average*	Existing Standard
WHO Guidelines	5-20 µg/m^3	
India (CPCB Expert Group)	16 µg/m^3 (5ppb) running annual average	31st Dec., 2005
	5 ug/m^3	To be reduced to 5 ug/m^3 by 31st Dec., 2010
India (CPCB Standard ,November 2009)	5 µg/m^3 – annual average	

* Prefer GC-MS (sample to be collected with canister or tube) or its equivalent method).

b. PAHs

These compounds are one of the seven organic air pollutants of concern, as identified by the EPA because of their persistence and tendency to bio-accumulate in the environment. PAHs are a group of approximately 10,000 compounds, a few of which are listed below. These compounds are highly lipid-soluble. Some PAHs can dissolve in water. PAHs can enter groundwater from ash, tar, or creosote that is improperly disposed in landfills.

Box 6 - Major PAH Compounds

Acenaphthylene($C_{10}H_8$)
Acenaphthene($C_{10}H_8$)
Fluorene($C_{10}H_8$)
Naphthalene ($C_{10}H_8$)
Phenanthrene ($C_{14}H_{10}$)
Anthracene ($C_{14}H_{10}$)
Fluoranthene ($C_{16}H_{10}$)
Pyrene ($C_{16}H_{10}$)
Chrysene ($C_{18}H_{12}$)
Benzo(a) anthracene ($C_{18}H_{12}$)
Benzo(b) fluoranthene ($C_{20}H_{12}$)
Benzo(k) fluoranthene ($C_{20}H_{12}$)
Coronene ($C_{24}H_{12}$)
Benzo(e) pyrene ($C_{20}H_{12}$)
Benzo(a) pyrene ($C_{20}H_{12}$)
Perylene ($C_{20}H_{12}$)
Benzo(ghi) perylene ($C_{22}H_{12}$)
Dibenzo(ah) anthracenes ($C_{22}H_{14}$)
Indeno(cd) pyrene ($C_{22}H_{12}$)

The ***sources*** of atmospheric PAHs are both natural and anthropogenic. The natural sources are forest fire, volcanic activities and bacterial decay of organic materials. The anthropogenic sources are industries, automobiles and households. In general, more PAHs form when materials burn at low temperatures, such as in wood fires or cigarettes, incomplete burning of carbon-containing materials like oil, wood, garbage or coal. High-temperature furnaces produce fewer PAHs. Below is a glimpse of the major sources.

- Combustion of fossil fuels (Coke oven, aluminium, iron and steel foundries and Thermal Power Plant)
- Coal tar and other fossil fuel processing & using industries (Petroleum refining, coke production, shell-oil and creosotes using industries)
- Automobile engine exhausts – both diesel and gasoline vehicles and Air crafts.
- Accidental spills from oil tankers and other ships
- Refuse burning and fire - Forest and prairie fires, Burning of Creosote and other wood preservative wastes and Rural and urban sewage sludge
- Other Sources - Tobacco and cigarette smoke, mothballs, skin creams and anti-dandruff shampoos blacktop,

Box 7 - Exposure to PAHs

Breathing cigarette smoke, auto emissions or industrial exhausts; people living near such sources (like major highways) or working at such places (like TPPs).

Drinking groundwater near disposal sites where construction wastes or ash are buried.

Eating Charcoal-broiled foods, especially meats, Shellfish living in contaminated water.

Touching - handling contaminated soil or bathing in contaminated water, using medicated skin cream or shampoo containing PAHs, may result in absorption through skin.

A person's reaction, on exposure to PAHs depends on several things, including individual health, heredity, previous exposure to chemicals including medicines, and personal habits such as smoking or drinking. A few routes of exposure are listed in the box.

Health Effects - Some PAHs are classified as potent carcinogens. The benzo (a) pyrene is referred to as “one of the most potent carcinogens known” **(Sutherland et al, 1995**). PAHs may be attached to dust or ash causing lung irritation. Skin contact with PAHs may cause redness, blistering, and peeling. These may penetrate into the bronchial epithelium cells where metabolism takes place. Chronic exposure may lead to Cancer; Reproductive Effects and problems in unborn babies’ development; Organ Systems damage (lungs, liver, skin, and kidneys); respiratory problems and behavioural effects.

Table 12 - Details of Quantification techniques used in various overseas studies

RN	**Sampling**			**Desorption**	**Analysis**					
	Device	**Sorbent**	**Flow rate**		**Device**	**Column**	**Detector**	**Carrier**	**Temp. prog**	**Injector**
Psai et al, 2004	Aerosol sampler with sorbent tube	XAD-2 (3.5g/0.5g)	2.0 L/min	Hexane + dichloromethane (1:1)	GC / GC-MS	Ultra2 (50m×0.32mm×0.17 µm)	MSD	-	50º C to 100º C @20º C /min;100º C to 290º C @3 º C /min	1µl
Yang et al, 2005	Pallflex filters	XAD-16 resin and PUF	-	Hexane + dichloromethane (1:1)	GC-MS	Ultra2 (50m×0.32mm×0.17 µm)	MSD	-	50º C to 100º C @20º C /min;100º C to 290º C @3 º C /min hold at 290º C for 40 min	1µl
Tavares et al, 2004)	SKC pump with glass catridge , filter	XAD-16 resin and PUF, Teflon filter	2.0 L/min	ACN + dichloromethane (3:1)	GC	DB1 (30m×0.25mm×0.25 µm)	FID (340º C)	-	80º C(1min) to 120º C@20º C/min to 340º C@7º C/min and held for 10 min	2µl
Castelleo et al, 2003	HVS and filters	-	1.0L/ min	Dichloromethane (ultrasonically30 min)	GC/MS	HP-5MS (30m×0.25mm×0.25 µm)	MSD	He	50º C to 300º C @8ºC /min	-
Kalberer et al 200	Quartz Filters	-	15 L/min	2ml of CS_2 (30-45 min)	Laser mass spectroscopy	-	-	-	-	-
Fang et al, 2004	Sampler with glass catridge	PUF and XAD-16	-	Hexane + dichloromethane (1:1)	GC	DB5 (30m×0.25mm×0.25 µm)	MSD	-	35º C held (3min) to 180ºC@25ºC /min (2min) to 200ºC@20ºC /min (10 min) to 300ºC@2ºC/ min (6.4min)	1µl
Swart	Sampler	XAD-4	84	Hexane +	GC	RTX5	FID	He	60º C (12min)	-

RN	Sampling			Desorption	Analysis					
	Device	Sorbent	Flow rate		Device	Column	Detector	Carrier	Temp. prog	Injector
zet al, 2003	with filter		l/min	dichloromethane (1:1)		(30m×0.28mmid×0.25µm)	250		increased @10º C /min to 140º C to 320º C (15min) @ 5º C /min	
Ngabe et al, 2003	Glass filters with plugs	PUF	0.3 m^3/hr	Hexane + dichloromethane	GC/MS	DB5 30m×0.25mm×0.25 µm)	MSD	He	100º C (1min) to 270ºC @8ºC/ min	-
Chan et al, 2003	Stainless steel adsorbent tubes	Tenax TA & carbisieve S-3	0.15 mL/min	Thermal Desorption	GC	HP-VOC capillary column (30m,0.32mm,0.5µm)	MSD	He	Oven temp. initially held at 35º C (2min) raised to 250º C @8º C /min(5min	
Busson et al, 2003	OVM passive sampler	Charcoal	-	2ml of CS2(30-45 min	GC	Voc AL m TM(105m,0.53mm,3.0µm)	FID, 250	He	31º C (2min) to 100 º C @5º C /min to 200º C @50º C /min	1µl
Young et al, 2002	Tubes	Carbopack Band carbosieve (1,3-butadiene tenax GR + carbotrap (7 other VOC)	40 mL/min	Thermal Desorption	GC	PLOT capillary column(50mm,0.32mm,5µm for butadiene) Stabil wax capillary column (50m,0.25mm for others)	MSD	-	-	-
Kwangsam et al, 2001	Summa canisters	-	10-15 mL / min	Cryogenic conc using liq. Air followed by revolatilization by hot water	GC	Ultra1 methyl silicone(50m,0.2mm	FID	H_2	-55º C (3min) to 40 º C @15º C /min to 150º C (15 min)@4º C /min to 195 º C @25º C /min	-
Chunming et al,2000	Tubes	GDX102	0.41 l/min	Thermal Desorption	GC	DB-5 fused silica(75m,0.25mm1d	FID 250	N_2	30º C (12min) increased @4º C /min to 160º C (18min)	-
Tyagi, 2004	High Volume Sampler / Respirable Dust Sampler	Whatmann EPM-2000 filter paper	1m^3/min	Toluene	GC and GC-MS	Ultra2 (25m×0.2mm×0.33µm)	FID & MSD	N_2 & He	120ºC (2 min) to 240ºC (3 min) @6ºC/ min to 290ºC @7ºC per min (7.86 min) , 40 min run time, inlet - 300ºC,FID 300 ºC Transfer 290ºC, MS source 230ºC, MS quadrapole-150ºC, mode-constant flow, column flow 1 ml/min, SIM mode	1µl

The present concentration of PAH in the air in various countries is mentioned in Table 12.

Table 13 - Levels of PAH in different cities of the world

City	**Bangkok** (ng/m^3)	**Bravo Murillo, Spain** (ng/m^3)	**Londrina, Brazil**(ng/m^3)	**Tainan, Taiwan** (ng/m^3)	**Ohio (Columbus) U.S.** (ng/m^3)		**Delhi** (ng/m^3)
Duration	June'96-Apr '97	Jan-Dec, 2001	Jan 14-29, 2002	Winter,2003	-		1993 - 2000
No.of samples	6	-	14	116	-		
Naphthalene	0.25	-	97.7±10.3	2570-13500	-		
Phenenthrene	0.3	0.205±0.059	348±32.7	88.9-532	20.22-122.6	37.37	0.2 – 0.9
Anthracene	0.21	0.047±0.031	31.1±6.137.9±7.9	36.6-202	2.14 - 21.79	2.72	0.2 – 1.4
Fluoranthene	0.25	1.049±0.323	-	33.7-584	10.93-27.47	13.44	0.6 – 1.9
Pyrene	0.13	0.381±0.144	39.8±8.9	42.4-229	5.04-8.55	7.67	0.7 – 2.9
Benzo(a)anthracene	1.06	0.457±0.104	1.4±0.3	30.8-92.5	0.42-2.35	1.28	1.1 – 3.7
Chrysene	1.12	0.633±0.301	3.8±0.8	-	0.70-5.5	2.36	1.6 – 3.5
Benzo(e)pyrene	2.47	-	-	71.1-136	0.23-2.06	1.67	2.2 – 5.4
Benzo(b)fluoranthene	0.94	-	-	78.0-977	-	-	1.0 – 6.3
Coronene	1.82	-	-	-	0.13-1.68	1.44	-
Indenol	0.71	-	-	22.5-80.4	0.24 - 2.25	1.27	1.0 – 8.4
Benzo(a)pyrene	1.7	0.341±0.163	-		0.07-2.75	1.38	1.9 – 3.5
Flourene	-	-	140.2±17.3	10.4 - 429	-	-	-
Reference	Oanh et al, 2000	Castellano et al, 2003	Tavares et al, 2004	Tsai et al, 2004	Somenath, 1992		Tyagi, 2004

Flow Chart 6 - Measurement Method of PAH (ISO, BIS, CPCB, Tyagi, 2004 Method) - Individual PAH compounds

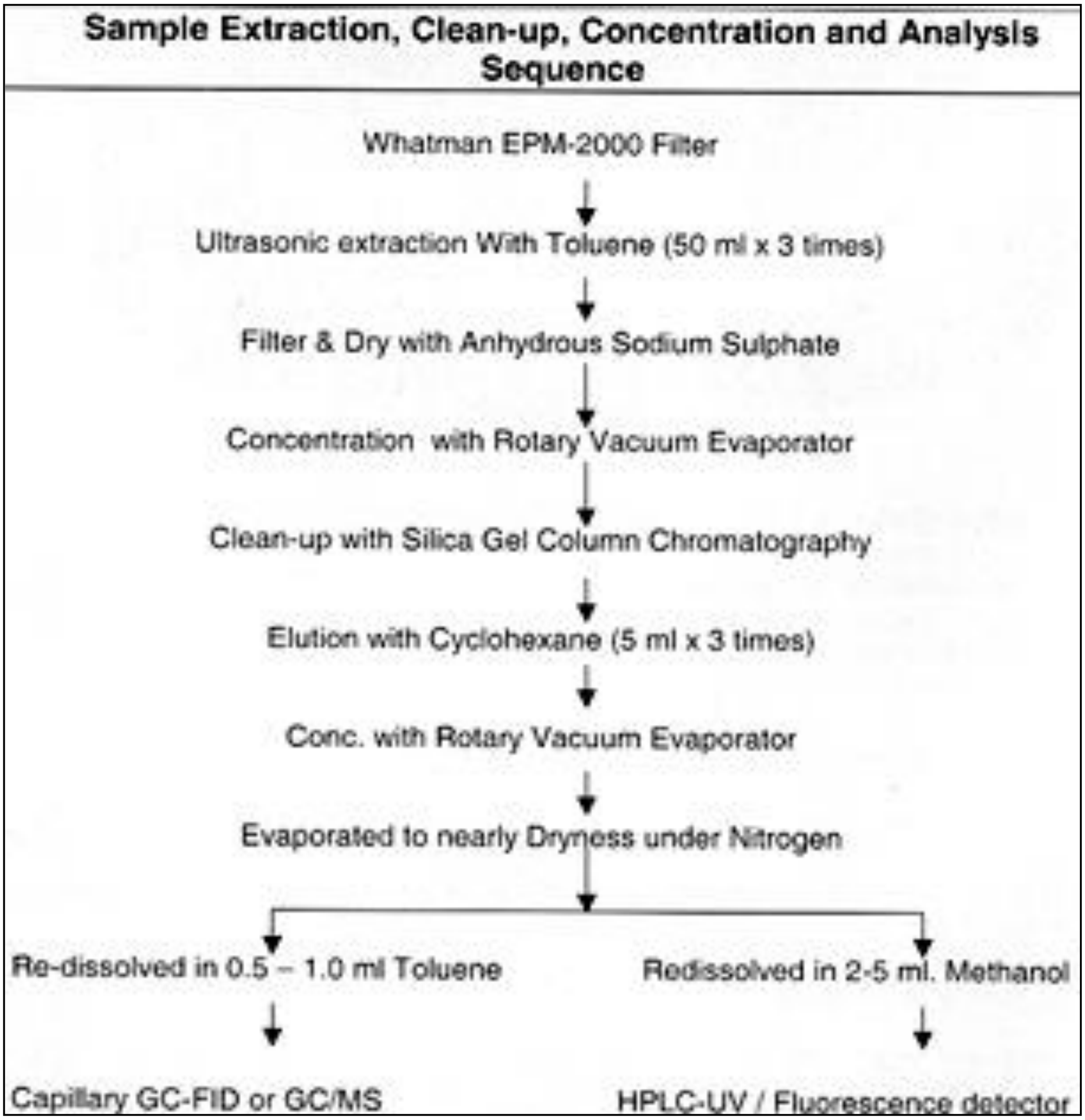


Table 14 - Ambient Air Quality Standard for PAHs as Benzo (a) Pyrene, i.e., B(a)P

Note : ** Reducing by 1 µg/m^{3}every year from 2005 to 2010.

Country	Limit value	Guide value
Netherlands	5 ng/m^3	0.5 ng/m^3
WHO-AQG		1.0 ng/m^3
India (CPCB Expert Group)	5 ng/m^{3**}	1 ng/m^3
India (CPCB Standard ,November,2009)	1ng/m^3 Annual Avg	

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CHAPTER 10

PERSISTANT ORGANIC POLLUTANTS (POPs)

As a consequence of rapid development, a significant amount of organic chemicals have been dispersed into the environment, but the long term biological effects of most are unknown **(Lubchenco, 1998)**. One group of such chemicals referred to as **persistent organic pollutants (POPs)** has been shown to exhibit potentially harmful effects in man and the environment. Persistent organic pollutants (POPs) are defined as organic substances, which possess toxic and bio-accumulative characteristics, are persistent and prone to long range transboundary atmospheric transport and depositions. In addition to being persistent, POPs are typically lipophillic, semi volatile, and toxic. Some of POPs have been deliberately produced by the industry for a wide variety of applications. Others are accidentally formed or eventually released as a byproduct from various activities, such as industrial or Combustion process **(Wania et al., 1999).** POPs are emitted into the environment as complex mixtures, such as Polychlorinated Biphenyls (PCBs) **(Breivik et al., 2002)** and PBDEs. The UN-ECE Protocol on POPs drafted in March 1998 has identified 16 most hazardous and persistent chemicals. Examples of POPs – DDT, PCBs, Dioxins and Furans, Hexa-chloro-benzene etc.

1) Poly Chlorinated Biphenyls (PCBs)

Polychlorinated-bi-Phenyls (PCBs) are a range of substances consisting of a biphenyl molecule with or without alkyl or aryl substituents, in which more than one chlorine atom is substituted in the biphenyl nucleus. Chlorination of the group can produce 209 possible chloro-biphenyls (congeners) substituted with 1-10 chlorine atoms. The chemical formula of PCBs can be represented as $C_{12}H_{10-n}Cl_n$. It is believed that PCBs do not occur naturally. PCBs are extremely persistent in humans; their elimination halve-lives are typically many years **(Shirai and Kissel, 1996)**. PCB concentration in air has been shown to be positively related to temperature with maximum concentrations being observed in summer **(Hoff et al., 1992; Hillery et al., 1997)**. The presence of poly chlorinated biphenyls in humans has attracted concern because of their potential teratogenic, carcinogenic, hormonal and immunological effects **(Nicholson and land-gan, 1994)**. PCBs are lipophillic with low solubility in water and very low vapour pressure, both of which generally decrease with increase in the degree of chlorination. They are excellent dielectrics, stable to thermal, chemical and biological degradation and are fire resistant. Commercial PCBs mixtures are light to dark yellow in color, do not crystallize even at low temperatures, but turn into solid resins and have high flash points.

PCBs are a kind of persistent organic pollutants which possess toxic properties, resist degradation, and accumulate in terrestrial and aquatic ecosystem. PCBs are used in heat transfer fluids, dielectric fluids (e.g. for capacitors of fluorescent lamp ballasts), electrical transformers, hydraulic fluids, paints, coatings, ceiling tiles, adhesives, flame retardant, vacuum pumps, pesticides and sealants. Joint sealing, usually based on polysulfide polymers may contain up to 30% PCB as plasticizer **(Balfanaz et al, 1993; Bent et al, 2000; Benthe et al, 1992; Bleeker et al, 2000; Burkhardt et al, 1990; Ewere et al, 1998; Fromme et al, 1996; Gabrio et al, 2000).** Volatilization from wastes containing PCBs, sewage sludge, spills & dredge spoilsis also a major source of exposure to these toxic compounds.

Table 15 - Physico-chemical properties of selected Polychlorinated Biphenyls

PCB compounds	**Water solubility** (mg/l) **at 25°C**	**Vapour Pressure** (torr)	**Density** (g/cm^3)	**Appearance**	**Boiling Point** (at 750 torr)
1016	0.42	4.0×10^{-4}	1.33	Clear oil	325-356
1221	0.59	6.7×10^{-3}	1.15	Clear oil	275-320
1232	0.45	4.1×10^{-3}	1.24	Clear oil	290-325
1242	0.24	4.1×10^{-3}	1.35	Clear oil	325-366
1248	0.054	4.9×10^{-4}	1.41	Clear oil	340-375
1254	0.021	7.7×10^{-5}	1.50	Light yellow viscous oil	365-390
1260	0.0027	4.0×10^{-5}	1.58	Light yellow sticky resin	385-420

Source: IARC (1978), WHO/EURO (1987)

Sources - People are primarily exposed to PCBs by consuming fish from contaminated water, but they can also be exposed through other foods. They are primarily excreted through bile and milk. Total PCB concentrations in indoor air up to 4200 ng/m^3 were detected. The average concentration of Aroclors in indoor air in the work places in United States ranged from 44 ng /m^3 to 240 ng / m^3. Outdoor levels of PCBs up to 18 ng/m^3 were observed .In indoor air of homes in United States, the average concentrations of PCBs in the kitchen ranged from 150 ng / m^3 to 500 ng / m^3 and in other rooms from 39 to 170 ng / m^3 **(C.P.C.B. Parivesh, 2004)**.

Health effects - Within a few hours of acute exposure to PCBs, skin rashes may occur. Exposure through ingestion is possible in the working environment through direct ingestion. Skin exposure is important in the case of long term exposure, even though the ambient concentration may be low.

Table 16 - Quantification Techniques for PCBs

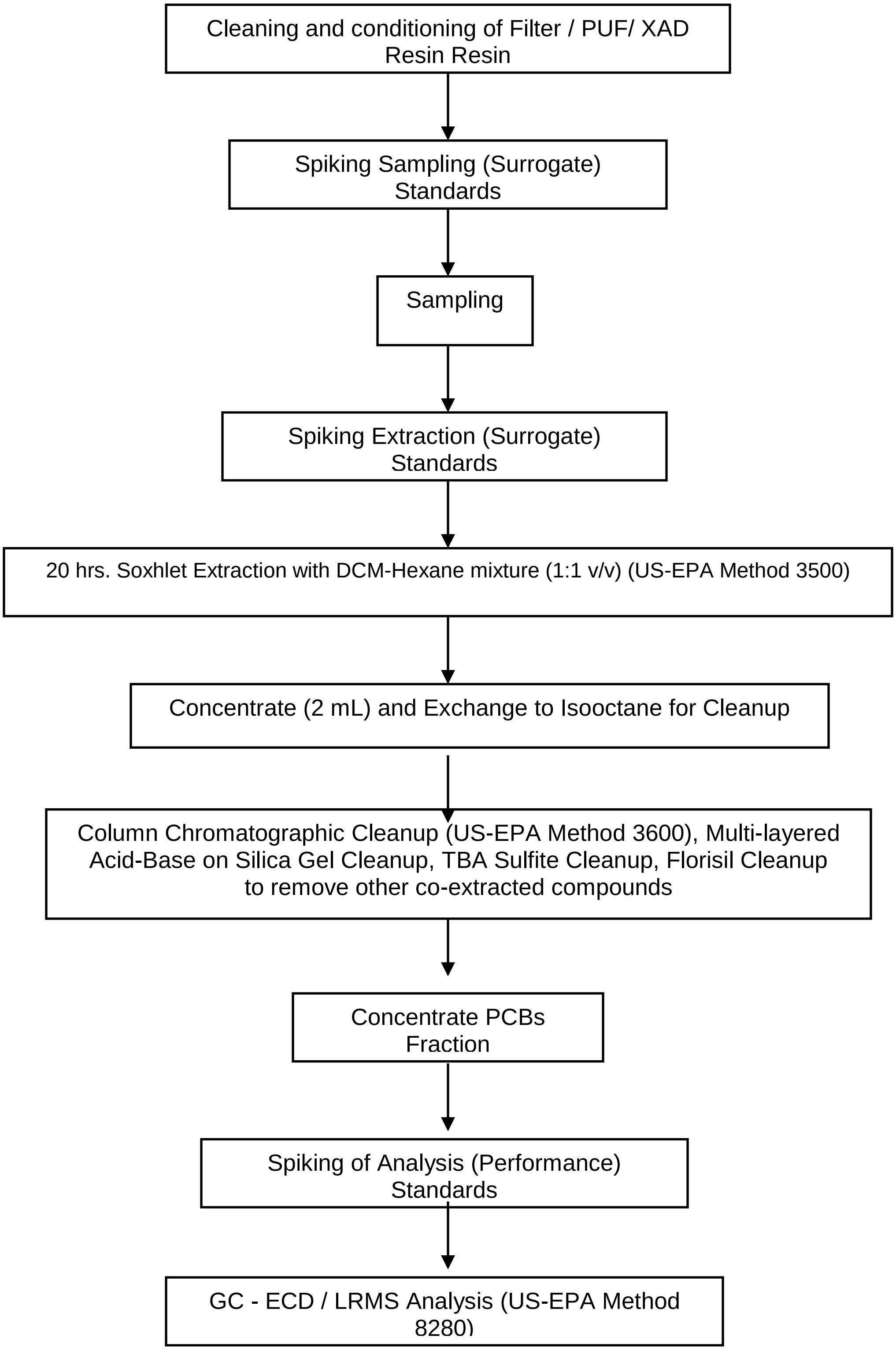
Sampling	**ASTM**	**USEPA**
Method A		TO-10A
Device	Cartridges	Cartridges
Medium	PUF (denity:0.225g/cm^3)	PUF (denity:0.225g/cm^3)
Flow rate	1-5 L/min	1-5 L/min
Duration	4-24 hrs	4-24 hr
Analysis	GC/ECD	GC/MD, GC/MS
Detection limit	1-50 ng/ml	0.001-50 µg/m^3

Levels - The levels of PCBs in the ambient air are 0.002 – 15 ng/m^3.

Table 17 - Concentration of total PCBs in water and sediment samples of Yamuna River and drains in Delhi

S.No.	**Sampling Locations**	**Total PCBs in sediments (ng/g)**	**Total PCBs in water (ng/L)**
	Yamuna river		
	River Yamuna at Palla	8.927	0.505
	River Yamuna at old Yamuna Bridge	1.140	0.190
	River Yamuna at Nizamuddin bridge	1.908	1.289
	River Yamuna at Okhla	0.641	1.926
	River Yamuna at Palwal	0.616	0.501
	Drains		
	Najafgarh Drain	8.300	1.476
	Civil Mill Drain	281.397	4.738
	Power House Drain	0.282	6.545
	Sen Nursing Home Drain	1.361	0.288
	Shahdara Drain	5.010	1.540

Flowchart 7 - Measurement method of PCBs (US-EPA and Canadian Methods)



The maximum permissible concentration of PCBs in ambient air, as fixed by the USEPA, is **0.5 mg/m^3**.

2) Dioxins and Furans

The **Polychlorinated Dibenzo-para-Dioxins** (PCDDs) and **Polychlorinated Dibenzo Furans** (PCDFs) are structurally related non-polar tricyclic halogenated aryl hydrocarbons poorly soluble in water. These are lipophillic compounds (having affinity towards lipids and fats) whose degree of lipophilicity increases with the degree of chlorine substitution in the parent molecule. These compounds are resistant to chemical breakdown through acid-base reaction, oxidation-reduction and even hydrolysis and the degree of stability of PCDDs and PCDFs also increase with degree of chlorine substitution in the parent molecule. All the isomers of dioxins and furans and dioxin like compounds are toxic but their toxicity potential varies widely among their different congeners and positional isomers. Only 7 out of 75 isomers of dioxin and 10 out of 135 isomers of furan exhibit critical toxic effects because of their chemical nature and property.

Structurally two oxygen atoms bind two benzene rings in Dibenzo Para-Dioxin to form tricyclic structure, whereas, in Dibenzofurans, one oxygen atom binds a biphenyl molecule to become tri-cyclic. There are eight substitution positions of chlorine in both dioxin and furan parent molecule, resulting into 75 PCDDs and 135 PCDFs positional isomers respectively, substituted with 1-8 chlorine atoms. For example, Mono-chloro di-benzo para-dioxin has two isomers and Mono-chloro Dibenzo-furan has four isomers.

These compounds do not occur naturally, nor are they produced intentionally. They are the byproducts of industrial and pollution control related operations barring a few catastrophic or accidental origins like volcanoes, forest fires and accidental fires. Dioxins are released into the ambient environment either directly along with emissions or indirectly through volatilization from land, water and resuspension of particulates. The sources of Dioxins & furans are listed in Flowchart No. 1.

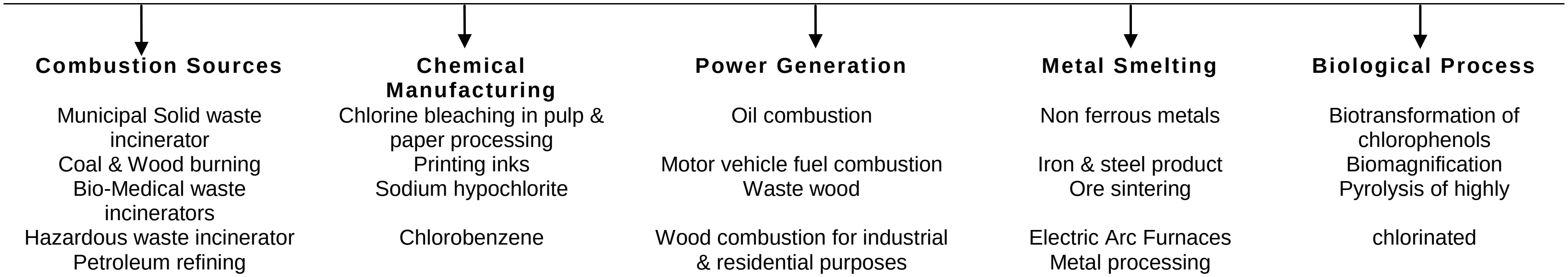
Short term exposure to high levels of dioxin may result in skin lesions, such as chlorance; patchy darkening of the skin, altered liver functions etc. in human beings. Chronic exposure may result in various type of cancer porphria – a disorder in enzyme synthesis which is marked by discoloration and increased fragility of the skin may occur on chronic exposure. Long term exposure is linked to impairment to immune system, nervous system, endocrine system and reproductive functions. Long term exposure even to low concentration of dioxin alters the reproductive functions including infertility, miscarriage, spontaneous abortion, congenital anomalies, and neonatal developmental abnormalities.

Table 18 - TCDDs and TCDFs in human adipose tissue (ng/Kg wet tissue) in various advanced countries 1989

PCDD & PCDF Isomers	Sweden	USA	Canada	Japan	North Vietnam	South Vietnam	Germany
PCDDs (Poly chlorinated di-benzo para dioxin)							
2,3,7,8 - TCDD	3.0	7.2	6.4	9.0	<2	28.0	150.0
1,2,3,7,8 - PCDD	10.0	11.1	10.0	15.0	<2	15.0	19.2
1,2,3,6,7,8 - HCDD	15.0	96	81.0	70.0	11.0	100.0	77.0
1,2,3,7,8,9 - HCDD	4.0	NA	NA	12.0	NA	NA	9.4
1,2,3,4,6,7,8 - HCDD	97.0	164	135	77.0	28.0	178.0	56.0
Octa – CDD	414.0	707	830	230.0	104.0	1256.0	267.0
PCDFs (Poly chlorinated di-benzo furan)							
2,3,7,8 - TCDF	3.9	NA	NA	9.0	NA	NA	0.9
1,2,3,7,8 – PCDF	54.0	14.3	15.0	25.0	13.0	21.0	44
1,2,3,4,7,8 – HCDF	6.0	NA	NA	15.0	NA	NA	10
1,2,3,6,7,8 – HCDF	5.0	31.3	16.0	14.0	13.0	58.0	6.7
2,3,4,6,7,8 – HCDF	2.0	NA	NA	8.0	NA	NA	3.8
1,2,3,4,6,7,8 – HCDF	11.0	16.5	30.0	NA	7.0	29.0	19.5
Octa – CDF	4.0	NA	NA	NA	NA	NA	1.0

NA – Data not available

Flowchart 8 - Sources of Dioxins and Furans



Combustion Sources

- Municipal Solid waste incinerator
- Coal & Wood burning
- Bio-Medical waste incinerators
- Hazardous waste incinerator
- Petroleum refining

Chemical Manufacturing

- Chlorine bleaching in pulp & paper processing
- Printing inks
- Sodium hypochlorite
- Chlorobenzene

Power Generation

- Oil combustion
- Motor vehicle fuel combustion
- Waste wood
- Wood combustion for industrial & residential purposes

Metal Smelting

- Non ferrous metals
- Iron & steel product
- Ore sintering
- Electric Arc Furnaces
- Metal processing

Biological Process

- Biotransformation of chlorophenols
- Biomagnification
- Pyrolysis of highly

  chlorinated

Table 19 - Levels of different dioxin and furan varieties in different areas

Monitoring sites	**Tetra - Isomers**		**Penta- Isomers**		**Hexa - Isomers**		**Hepta - Isomers**		**Octa - Isomers**		**Total**	
	CDDs	CDFs	CDDs	CDFs	CDDs	CDFs	CDDs	CDFs	CDDs	CDFs	CDDs	CDFs
Urban Area	0.10	0.36	0.07	0.51	0.74	0.18	0.60	0.10	0.37	0.10	1.88	1.25
Traffic tunnel	0.22	6.2	1.3	4.1	2.7	1.1	3.4	1.20	6.4	1.0	14.02	13.6
Downwind of MSW incinerator	0.21	4.9	2.4	5.0	5.3	2.2	5.3	2.0	7.40	0.78	20.61	14.88
Vicinity of dump site and metal refinery	1.5	3.3	5.0	10.0	24.0	9.5	15.0	5.0	40.0	7.0	85.5	34.8
Street when clean air blowing	0.15	0.32	0.2	0.47	0.1	0.18	0.38	0.10	0.29	0.15	1.12	1.22
Street at inversion	0.35	2.0	0.84	2.5	0.52	0.80	2.90	1.1	1.90	0.48	6.51	6.88
Rural research station (during wind blowing from sea)	0.009	0.054	0.031	0.085	0.032	0.07	0.14	0.12	0.064	0.10	0.276	0.429
Rural research station (during wind blowing from city)	0.13	0.49	0.28	0.60	0.19	0.31	1.0	0.50	0.54	0.44	2.54	2.34

Flowchart 9 - Measurement Method of Dioxins & Furans (US-EPA and Canadian Methods)

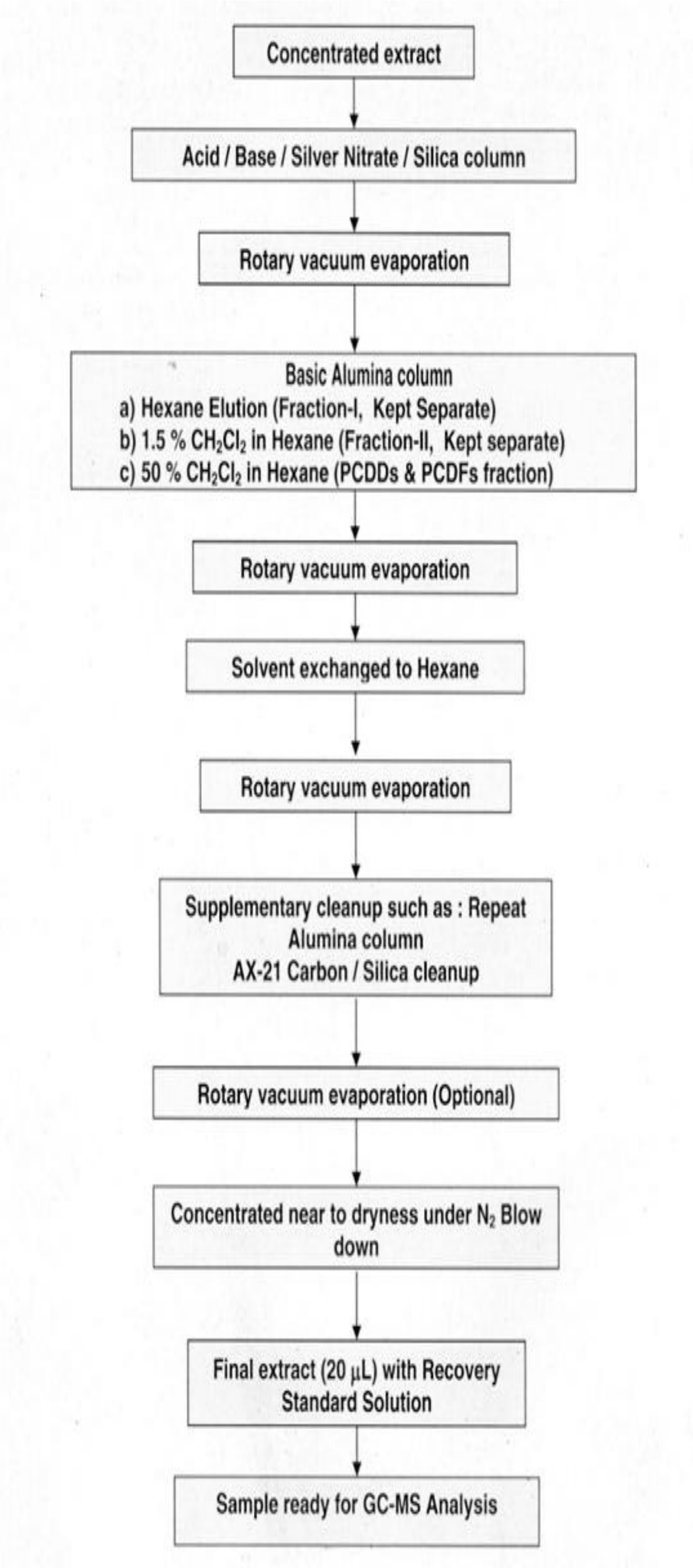


Table 20 - International Environmental Standards for Dioxins and Furans

Country	Sources	Standards for Dioxin and Furan
Hong Kong	Municipal Solid Waste Incinerator	13 ng/ m^3 (Total mass)
	Chemical Waste Treatment	0.1 ng I-TEQ / m^3
USA	Municipal Solid Waste Incinerator (more than 35 Tonnes / day)	13 ng/ m^3 (Total mass) about 0.1 to 0.3 ng I-TEQ / m^3
	Hazardous waste incinerator	0.2 ng I-TEQ / m^3
European Union	Waste Incinerators	0.1 ng I-TEQ / m^3
Japan	Capacity more than 4 Tonnes / hour Capacity from 2 to 4 Tonnes / hour Capacity less than 2 Tonnes / hour	0.1 ng I-TEQ / m^3 1.0 ng I-TEQ / m^3 5.0 ng I-TEQ / m^3
Canada	All New incinerators	0.08 ng I-TEQ / m^3

CPCB has recorded a concentration of PCDD/Fs levels (WHO-TEQ-pg/m^3) in Airborne Particulate Matter at ITO, B.S.Zafar Marg , Delhi between 0.056 & 0.593 pg/ WHO-TEQ-pg/m^3 (or 563 to 3592 pg WHO-TEQ-pg/g**)**

2) Pesticides

'Pesticides' includes compounds that can be present in both agricultural and non-agricultural formulations. Pesticides are used to reduce crop loss from disease and pest (plant and insect) attack, both before and after harvest. They are also used for public health to control various human pests and disease carriers. These species may be present as either a vapour or a mixture of vapour and airborne particles. The term 'pesticides' has a very broad definition which embraces herbicides, fungicides, insecticides, rodenticides, soil-sterilants, wood preservatives and surface biocides among others. It can also include substances like growth regulators, defoliants, desiccants, fumigants and repellents/attractants.

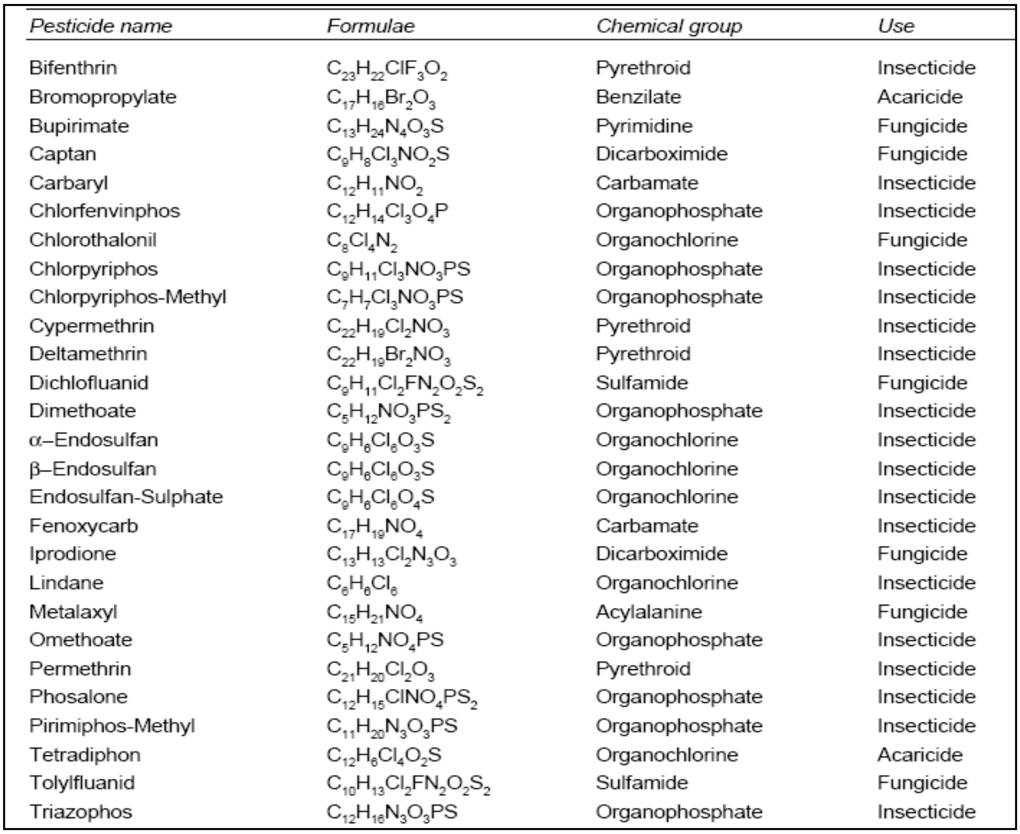
Organo-chloro pesticides are typical persistent organic pollutants. In the past decades, it has been successfully illustrated that POPs can migrate to Polar Regions through evaporation, atmospheric transport, and deposition **(USEPA, 2000; Lee et al., 1999)**. For this reason research on the atmospheric concentrations of OC pesticides is important.

Agricultural pesticides are released into the atmosphere by spray drift, post application volatilization, and wind erosion of soil. Among these, volatilization can remove large fractions of the pesticide initially applied to the field **(Draxer et al., 2003)**. Pesticide movement away from the release site in the air is usually called drift. Pesticide particles, dusts, spray droplets, and vapors all may be carried offsite in the air.

Particles and droplets - Lightweight particles, such as dust and wettable powders, are easily carried by moving air. Granules and pellets are much heavier and tend to settle out of air quickly. Small spray droplets also are easily carried in air currents. High-pressure and fine nozzles produce very small spray droplets that are very likely to drift. Lower pressure and coarse nozzles produce larger droplets with less drift potential. The likelihood that pesticide particles and spray droplets will drift offsite depends partly on the way they are released. Pesticides released close to the ground or floors are not as likely to be caught up in air currents as those released from a greater height. Pesticides applied in an upward direction or from an aircraft are the most likely to be carried on air currents.

Vapours - Pesticide vapours move about easily in air. Fumigant pesticides are intended to form a vapour when they are released. People using fumigants must take precautions to make sure the fumigant remains in a sealed container until it is released into the application site, which also must be sealed to prevent the vapour from escaping. Some non-fumigant pesticides also can vaporize and escape into the air.

Box 8 - Major Pesticides



Pesticide name	*Formulae*	*Chemical group*	*Use*
Bifenthrin	$C_{23}H_{22}ClF_3O_2$	Pyrethroid	Insecticide
Bromopropylate	$C_{17}H_{16}Br_2O_3$	Benzilate	Acaricide
Bupirimate	$C_{13}H_{24}N_4O_3S$	Pyrimidine	Fungicide
Captan	$C_9H_8Cl_3NO_2S$	Dicarboximide	Fungicide
Carbaryl	$C_{12}H_{11}NO_2$	Carbamate	Insecticide
Chlorfenvinphos	$C_{12}H_{14}Cl_3O_4P$	Organophosphate	Insecticide
Chlorothalonil	$C_8Cl_4N_2$	Organochlorine	Fungicide
Chlorpyriphos	$C_9H_{11}Cl_3NO_3PS$	Organophosphate	Insecticide
Chlorpyriphos-Methyl	$C_7H_7Cl_3NO_3PS$	Organophosphate	Insecticide
Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	Pyrethroid	Insecticide
Deltamethrin	$C_{22}H_{19}Br_2NO_3$	Pyrethroid	Insecticide
Dichlofluanid	$C_9H_{11}Cl_2FN_2O_2S_2$	Sulfamide	Fungicide
Dimethoate	$C_5H_{12}NO_3PS_2$	Organophosphate	Insecticide
α–Endosulfan	$C_9H_6Cl_6O_3S$	Organochlorine	Insecticide
β–Endosulfan	$C_9H_6Cl_6O_3S$	Organochlorine	Insecticide
Endosulfan-Sulphate	$C_9H_6Cl_6O_4S$	Organochlorine	Insecticide
Fenoxycarb	$C_{17}H_{19}NO_4$	Carbamate	Insecticide
Iprodione	$C_{13}H_{13}Cl_2N_3O_3$	Dicarboximide	Fungicide
Lindane	$C_6H_6Cl_6$	Organochlorine	Insecticide
Metalaxyl	$C_{15}H_{21}NO_4$	Acylalanine	Fungicide
Omethoate	$C_5H_{12}NO_4PS$	Organophosphate	Insecticide
Permethrin	$C_{21}H_{20}Cl_2O_3$	Pyrethroid	Insecticide
Phosalone	$C_{12}H_{15}ClNO_4PS_2$	Organophosphate	Insecticide
Pirimiphos-Methyl	$C_{11}H_{20}N_3O_3PS$	Organophosphate	Insecticide
Tetradiphon	$C_{12}H_6Cl_4O_2S$	Organochlorine	Acaricide
Tolylfluanid	$C_{10}H_{13}Cl_2FN_2O_2S_2$	Sulfamide	Fungicide
Triazophos	$C_{12}H_{16}N_3O_3PS$	Organophosphate	Insecticide

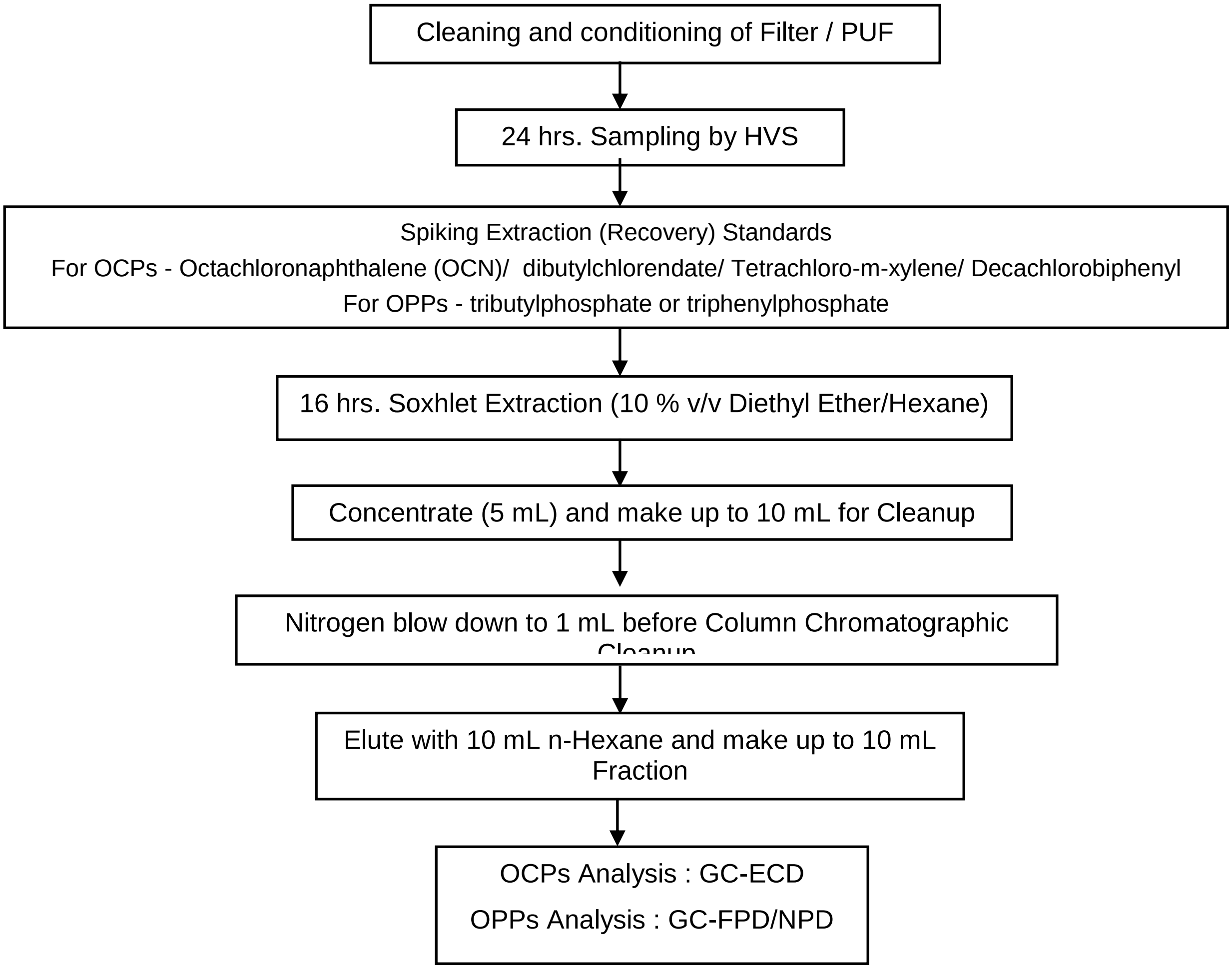
Health effects

Pesticides are hazardous to health causing many possible complex symptoms resulting from exposure. They may cause symptoms such as headaches, dermatitis, muscle twitches, allergies, reproductive damage, cancer and even death. A recent review has put pesticide poisoning in perspective: ‘The primary hazard of pesticide exposure is the development of acute toxic reactions as a result of dermal contact with, or inhalation of “a relatively large dose”. Over-exposure by skin contact or breathing in pesticides can lead to toxic effects.

Table 21 - Pesticides (ng/l) analysed in CPCB's groundwater survey in the problem areas 2001 – 2002

S.No.	Problem Area	Dieldrin	Lindane	Aldrin	DDT	Endo - sulphan	BHC	Hepta - chlor
1.	**Durgapur**	NT - 39.3	NT-494.1	NT- 61.2	12.3-476	NT - 134	NT - 1904	NT-44.1
2.	**Howrah**	NT-12.3	NT-116.4	NT-21.0	NT-81.6	NT-12.3	NT-201.3	NT-13.8
3.	**Dhanbad**	NT -64.8	NT-425.4	NT-77.4	NT-596.2	NT-243	NT-1516.8	NT-62.4
4.	**Singrauli**	NT	NT-277.9	NT	NT-216.6	ND	ND	ND

Flowchart 10 - Measurement Method of Pesticides in Air



(US-EPA Method TO-4A)

Bureau of Indian Standards, in 1991, has fixed the maximum desirable concentration of pesticides in air to be nil and the permissible limit to be **0.001 ppm**.

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CHAPTER 11

CARBONYLS

Aldehydes and Ketones belong to a class of compounds called carbonyl compounds. The most common carbonyls in air include formaldehyde, acetaldehyde, and acetone. Carbonyls in air are collected by drawing air through a cartridge impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH), which is very reactive toward carbonyls. The resulting products (hydrazones) in the cartridge are measured in the laboratory using high performance liquid chromatography to determine the levels of the carbonyl compounds originally present in air.

Health Effects - irritation of the mucosa in the eyes and upper respiratory tract, asthma-like symptoms, nasal or nasopharyngeal tumours, Cutaneous erythema, liver damage, facial flushing, and developmental effects. Acetone vapour can cause CNS depression, cardio-respiratory failure and death. Females exposed to atmospheric concentrations of 1000 ppm acetone were reported to suffer menstrual irregularities.

Quantification Techniques - The most used method is based on the reaction with 2,4-dinitrophenyl hydrazine (DNPH) absorbed on silica particles **(ASTM, 1992)**. Formed hydrazones can be analyzed and quantified by HPLC-UV after liquid extraction of DNPH coated particles. Very volatile carbonyls (such as formaldehyde, acetaldehyde and acetone) can be detected at levels of 0.4 ppbv on 60 l air samples. Components larger than pentanal require, instead, a volume of several hundred liters to meet the sensitivity a!orded by HPLC-UV **(Grosjean et al., 1996)**. Collection of semi-volatile carbonyls on light adsorbents (such Tenax and graphitic carbons), followed by GC-MS after thermal desorption of the sample, represents a valid alternative to HPLC}MS **(Helmig and Greenberg, 1994; Helmig et al., 1996; Ciccioli et al., 1993a, b; Brancaleoni et al., 1999)** but provides reliable results only for components heavier than C5. While the front traps are analyzed by GC-MS after thermal desorption, back-up cartridges are analyzed by HPLC-UV after liquid extraction. The method has been tested through laboratory and field experiments.

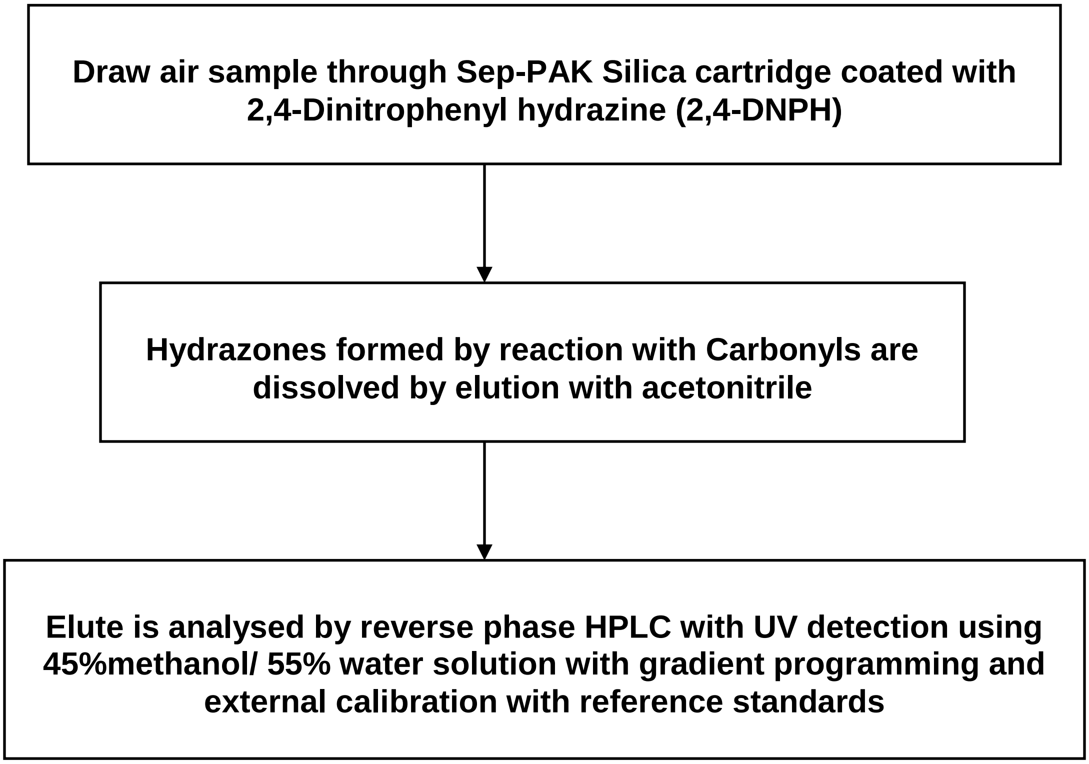
Table 22 – Quantification Techniques (λ = wavelength)

RN	Sampling			Desorption	Analysis					
	Device	Sorbent	Flow rate		Device	Column	Detector	Mobile Phase	Flow rate (mobile phase)	injector
1	catridges	DNPH	1-2 L/min	Acetonitrile	HPLC/ UV	Hypersil ODS column(150mm×4mm, 5µm)	PD set at λ= 360nm		1.5mL/min	20µl
2	Siica gel catridges	DNPH	0.8-1.2 l/min	ACN(5ml)	HPLC/ UV	SB- C18 (250mm×4.6mm, 5µm)	PD set at λ= 360nm		1.0ml/min	20µl
3	DSD catridges	DNPH	Diffusive sampling	ACN	HPLC	UV stainless steel tube packed with zorbax250mm×4.6mm,5µm	photodiode array detector	ACN +water (40+60v/v)	1.5ml/min	20µl
4	C-18 resin catridges	DNPH	1.0 L/min	ACN	HPLC/UV	Chrmopack C18 column (250mm×4.6mm, 5µm)	PD set at λ= 360nm			25µl

Table 23 – Levels of Carbonyl Compounds

Compounds	**Method-DSD-DNPH/HPLC (Uchiyama et al, 2004)**		**Carbon/Sep pak DNPH-GC-MS & HPLC (Possanzini et al, 2000)**		**Method TO11 (Feng et al, 2004)**	**Carbon/Sep pak DNPH-GC-MS & HPLC (Possanzini et al, 2000)**		
	LOD	Concentration	MDL(carbon)	MDL(SepPak)	Conc. GM^a+GSD^b	Conc. of C	Conc. DNPH	Conc.DNPH/KI
Formaldehyde	0.024	27	-	30	12.37±7.33	n.q	5.8	5.6
Acetaldehyde	0.026	27	1	50	6.9±4.76	0.3	4.7	5.3
Acetone	0.029	36	1	60	-	0.4	5.9	6.1
Acrolein	0.025	0.2	-	-	-	-	-	-
Propanal	0.029	2.2	1	50	1.18±0.95	<0.06	0.3	0.3
Crotonaldehyde	0.022	0.3	-	-	0.40±0.26	-	-	-
2-Butanone	0.027	16	-	-	5.29±6.12	-	-	-
Butyraldehyde	0.030	2.5	1.2	80	1.10±2.93	0.5	<0.5	<0.5
Cyclohexanone	0.028	3.0	-	-	1.67±2.54	-	-	-
Benzaldehyde	0.033	3.4	-	-	1.00±0.62	-	-	-
Isopentanal	0.026	0.7	-	-	0.37±0.25	-	-	-
Pentanal	0.031	2.6	1.2	35	0.35±0.29	0.2	<0.2	<0.2
o-Tolualdehyde	0.025	4.0	-	-	-	-	-	-
m,p-tolualdehyde	0.042	2.1	-	-	0.30±0.57	-	-	-
Hexanal	0.030	8.8	1.5	40	0.70±0.45	0.4-	<0.2	0.5
2,5-DMBA	0.023	1.6	-	-	0.64±0.06	-	-	-

Flowchart 11- Measurement Method of Carbonyls (US-EPA and Canadian Methods)



Draw air sample through Sep-PAK Silica cartridge coated with 2,4-Dinitrophenyl hydrazine (2,4-DNPH)

Hydrazones formed by reaction with Carbonyls are dissolved by elution with acetonitrile

Elute is analysed by reverse phase HPLC with UV detection using 45%methanol/ 55% water solution with gradient programming and external calibration with reference standards

* * *

CHAPTER 12

METALS

Lead

Lead is a soft, heavy, toxic and malleable metal that has atomic number 82. It is bluish white when freshly cut but tarnishes to dull gray when exposed to air. Lead is used in building construction, lead-acid batteries, bullets and shot, and is part of solder, pewter, and fusible alloys. The metal has poor electrical conductivity.

Sources

Lead-acid battery used extensively in car batteries, Lead-based paint, soil, lead solders in household water works, Lead smelters, Food and liquids stored in lead crystal or lead-glazed pottery or porcelain, coloring element in ceramic glazes (red & yellow) , etc. Tetraethyl lead was used in leaded fuels to reduce engine knocking.

Box 9 - Tetraethyl Lead

TEL was once used extensively as an additive in gasoline (petrol) for its ability to increase the fuel's octane rating (that is, to prevent knocking in the engine) thus allowing the use of higher compression ratios for greater efficiency and power. This additive was stopped from being used in the late 20th century, chiefly because of the realization that it released lead in the ambient air which can pose a grave health problem. There was one more reason for the abandonment of TEL as an anti-knocking agent which was its negative influence on the catalytic converter. TEL is still used in aviation gasoline and is also still available from a limited number of outlets as a fuel additive, mostly for owners of classic and vintage cars and motorcycles. Lead free petrol was introduced on September 1, 1998 in Delhi which started a total phasing out of Lead in petrol in the region.

Health effects

Lead can affect almost every organ and system in your body. The most sensitive is the central nervous system, particularly in children.

Exposure to lead is more dangerous for young and unborn children.

Children - Damage to the brain and nervous system, Behavior and learning problems (such as hyperactivity), Slowed growth, Hearing problems, Headaches

Adults - Difficulties during pregnancy, Other reproductive problems (in both men and women), High blood pressure, Digestive problems, Nerve disorders, Memory and concentration problems , Muscle and joint pain and also affects the immune system.

Table 24 – Pb in air in Indian cities

CITY	LEVELS
Mumbai	0.02 – 0.83
Bangalore	0.02 – 0.15
Nagpur	0.04 – 0.68
Jaipur	0.02 – 0.26
Chandigarh	0.02 – 0.22
Kanpur	0.10 – 1.41
Coimbatore	0.02 – 0.15

Source: Sadasivan et al. ind. J.Environ.Hlth., 1987.

Table 25 – Comparison of Pb levels in air in Delhi

Time Period	Range (ng/m^3)	Mean concentration
July'84–June'85	46 - 277	161
September1997	80 – 171	110
September1998	18 – 71	43
CPCB Standard		500 ng/m^3

Source: Central Pollution Control Board, Delhi, India

Measurement Method - Lead is measured with the help of Atomic Absorption Spectroscopy (as given in Chapter 6).

An important proportion of the lead may be removed through sedimentation (Atkins, 1969) but the most efficient **clearing mechanism** is probably rain (Ter Haar et al., 1967). The permissible limit of lead in ambient air is **0.75 µg/m^3 for sensitive areas and is 1.0 µg/m^3 for residential areas**.

Mercury

Mercury is a natural trace element which exists as a liquid at room temperature in its metallic form. Its vapour pressure is sufficiently high to yield hazardous concentrations of vapour at temperatures normally encountered both indoors and outdoors under most climatic conditions.

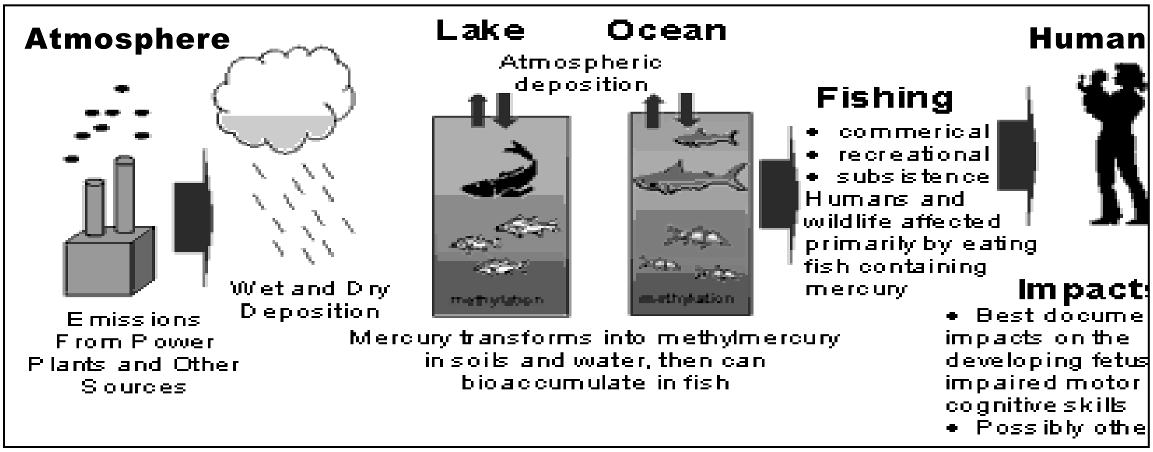
Typically, mercury is released into the atmosphere in one of three forms:

- elemental mercury: can travel a range of distances, may remain in the atmosphere up to one year and may travel globally before undergoing transformation
- particle-bound mercury: can fall out of the air over a range of distances
- oxidized mercury (sometimes called ionic or reactive gaseous mercury (RGM)): found predominantly in water-soluble forms, which may be deposited at a range of distances from

sources depending on a variety of factors including topographic and meteorological conditions downwind of a source.

2. Exposure to Mercury occurs when elemental mercury is spilled or products that contain elemental mercury break and expose mercury to the air, particularly in warm or poorly-ventilated indoor spaces.
3. ***Sources*** **–** Hg is released into the environment by nearly all coal power plants, municipal and medical incinerators. Mercury is also emitted to the air from natural sources, such as volcanoes.
4. chloralkali plants, electrical equipment, paints, measurements and control systems, such as thermometers and blood pressure meters, agriculture, dental, laboratory and other uses including military uses as detonators.
5. ***Health Effects*** - Elemental (metallic) mercury primarily causes health effects when it is breathed as a vapor where it can be absorbed through the lungs. Symptoms include these: tremors; emotional changes (e.g., mood swings, irritability, nervousness, excessive shyness); insomnia; neuromuscular changes (such as weakness, muscle atrophy, twitching); headaches; disturbances in sensations; changes in nerve responses; performance deficits on tests of cognitive function. At higher exposures there may be kidney effects, respiratory failure and death. High exposures to inorganic mercury may result in damage to the gastrointestinal tract, the nervous system, and the kidneys. Both inorganic and organic mercury compounds are absorbed through the gastrointestinal tract and affect other systems via this route. However, organic mercury compounds are more readily absorbed via ingestion than inorganic mercury compounds. Symptoms of high exposures to inorganic mercury include: skin rashes and dermatitis; mood swings; memory loss; mental disturbances; and muscle weakness. USEPA has concluded that mercury chloride and methylmercury are possible human carcinogens.

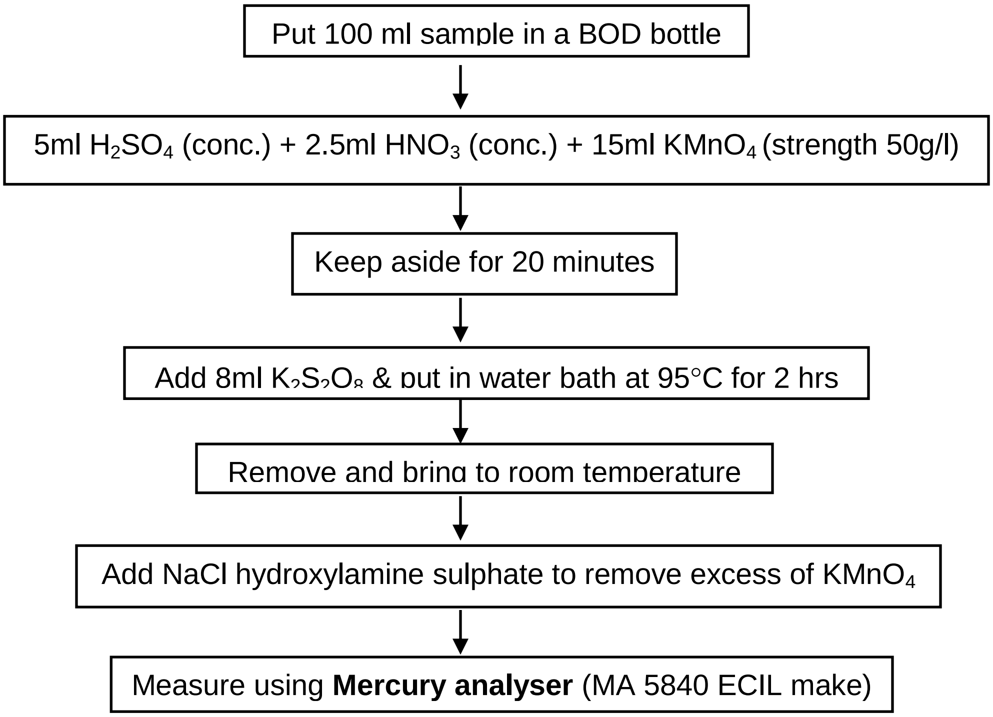
Fig 7 –Life Cycle of Mercury in the Environment



6. Levels of mercury in air are found to be in the range of 20 – 60 ng/ m^3.

7. ***Measurement method*** - The following flowchart depicts the procedure used to analyse mercury.

Flowchart 12 - Measurement Method of Mercury *(EPA method)*



Put 100 ml sample in a BOD bottle

5ml H_2SO_4 (conc.) + 2.5ml HNO_3 (conc.) + 15ml $KMnO_4$ (strength 50g/l)

Keep aside for 20 minutes

Add 8ml $K_2S_2O_8$ & put in water bath at 95°C for 2 hrs

Remove and bring to room temperature

Add NaCl hydroxylamine sulphate to remove excess of $KMnO_4$

Measure using **Mercury analyser** (MA 5840 ECIL make)

The maximum permissible value as given by the WHO is **0.05 mg/ m^3**.

Arsenic

Arsenic is a naturally occurring element with atomic number 33. This is a notoriously poisonous metalloid that has many allotropic forms; yellow, black and grey are a few that are regularly seen. Pure arsenic is a gray metal-like material usually found combined with other elements such as oxygen, chlorine, and sulphur. Arsenic and its compounds are used as pesticides, herbicides, insecticides and various alloys. Arsenic in animals and plants combines with carbon and hydrogen to form organic arsenic compounds. Most inorganic and organic arsenic compounds are white or colorless powders that do not evaporate. They have no smell, and most have no special taste. Most arsenic compounds can also dissolve in water. Arsenic cannot be destroyed in the environment. It can only change its form. Arsenic in air will settle to the ground or is washed out of the air by rain. Many arsenic compounds can dissolve in water.

Sources - Lead hydrogen arsenate has been used, well into the 20th century, as an insecticide on fruit trees (resulting in neurological damage to those working the sprayers), and Scheele's Green has even been recorded in the 19th century as a coloring agent in sweets. Inorganic arsenic occurs naturally in many kinds of rock, especially in ores that contain copper or lead. When these ores are heated at smelters to get the copper or lead, most of the arsenic enters the air as a fine dust. Smelters collect this dust and purify the arsenic for several uses. But once in the air, the arsenic particles travel with the wind for a while and then settle back to the ground. Thus, arsenic can get into lakes, rivers, or underground water by dissolving in rain or snow, or through the discharge of industrial wastes. Some of the arsenic will stick to the sediment on the bottom of the lake or river, and some will be carried along by the water. The main use is as a preservative for wood to make it resistant to rotting and decay. Inorganic arsenic compounds are also used to make several types of insect killers and weed killers are mainly used to preserve wood. Organic arsenic compounds are used as pesticides, primarily on cotton plants. Fish and shellfish can accumulate arsenic, but the arsenic in fish is mostly in a form that is not harmful. Eating food, drinking water, or breathing air containing arsenic, working in Arsenic using industries, smoke from wood treated with arsenic, living near uncontrolled hazardous waste sites containing arsenic, living in areas with unusually high natural levels of arsenic in rock are a few important sources of the metal. In the past, several kinds of products used in the home (rat poison, ant poison, weed killer, some types of medicines) had arsenic in them.

Health effects of inorganic arsenic are sore throat or irritated lungs, nausea, vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, a sensation of "pins and needles" in hands and feet, redness and swelling of the skin and even death. central and peripheral nervous system disorders are a common occuring amongst workers in Arsenic rich environment. Long term exposure to inorganic arsenic are peripheral neuropathy, darkening of the skin and the appearance of small "corns" or "warts" on the palms, soles, and torso and liver or kidney damage in humans. Several studies have shown that inorganic arsenic can increase the risk of lung cancer, skin cancer, bladder cancer, liver cancer, kidney cancer, and prostate cancer. Organic arsenic compounds are less toxic than inorganic arsenic compounds. Arsenic and many of its compounds are especially potent poisons.

Arsenic kills by inhibition of the metabolic enzyme lipothiamide pyrophosphatase, leading to death from multi-system organ failure. The IARC recognizes arsenic and arsenic compounds as group 1 carcinogens, and the EU lists *arsenic trioxide, arsenic pentoxide and arsenate salts as category 1 carcinogens.* Chronic arsenic poisoning from drinking water causes a disease known as *Arsenicosis*.

Table 26 - Concentrations of Arsenic in Ambient Air

Location	**Sampling period**	**Particle size and/or species**	**Concentration (ng/m^3)**	**Reference**
Antarctica	NS		0.019	Brimblecombe (1979)
Antarctic Ocean	1988–1989	As_i	0.05 (0.01–0.2)	Nakamura et al. (1990)
	1988–1989	As_o	0.002 (single sample)	Nakamura et al. (1990)
North Pacific Ocean	1981–1987	As_i	0.1 (0.01–0.95)	Nakamura et al. (1990)
	1981–1987	As_o	0.008 (0.001–0.03)	Nakamura et al. (1990)
North Atlantic Ocean	1989		0.1 (0.01–0.45)	Nakamura et al. (1990)
	1989	As_o	0.007 (0.001–0.3)	Nakamura et al. (1990)
Baltic Sea	1985		1.1 (0.3–3.7)	Häsänen et al. (1990)
Mid-Atlantic coast, USA	1985–1986		1.05	Scudlark & Church (1988)
Continental shelf waters, south-eastern USA	1975–1976	particulate	1.7 (0.2–4.3)	Waslenchuk (1978)
Northern Chesapeake Bay, USA	1990–1991	<10 µm	0.66 (0.11–1.96)	Wu et al. (1994)
Rural US sites (National Parks)	1979–1981	0.45 µm	< 1.6–2.3 (range of means)	Davidson et al. (1985)
Midwestern USA	1990		1.6 (0.7–2.5)	Burkhard et al. (1994)
Natural geysers, northern California, USA	1989	As (III)	0.22 & 0.54 (0.06–3.08)	Solomon et al. (1993)
		As (V)	0.46 (0.08–1.3) & 2.29 (0.7–6.54)	Solomon et al. (1993)
Bagauda, Nigeria	1976		0.6	Beavington & Cawse (1978)
Pelindaba, South Africa	1976		1.7	Beavington & Cawse (1978)
Chilton, United Kingdom	1976		4.2	Beavington & Cawse (1978)
Rural sites, United Kingdom	1972–1973		1.5–2.5 (range of means)	Peirson et al. (1974)
Rural area near Thessaloniki, Greece	1989–1990		2.7	Misaelides et al. (1993)
Birkenes, Norway	1978–1979	particulate	1.2 (0.02–12)	Amundsen et al. (1992)
	1985–1986	particulate	0.63 (< 0.04–4.6)	Amundsen et al. (1992)

As_i = inorganic As; As_o = organic As; NS = not stated

Measurement Method - There are a variety of instrumental techniques for the determination of arsenic. These include AAS, AFS, ICP-AES, ICP-MS and voltammetry. Some of these (e.g. ICP-MS) can serve as element-specific detectors when coupled to chromatographic separation techniques (e.g. HPLC and GC). Arsenic is generally measured using the Atomic Absorption spectroscopy method with Vapour Generator Assembly (VGA) also attached to the AAS. Arsenic is given to the AAS in the form of AsH_3 vapours generated by the VGA. For this the water/ soil sample containing Arsenic is digested (acid digestion), filtered and then inserted into the AAS system.

The EPA arsenic drinking water standard is **0.01 ppm** (10 ppb). The Occupational Safety and Health Administration has set limits of **10 μg/m^3** of workplace air. The WHO has prescribed a maximum permissible limit of **10 ppb** in drinking water.

Analysis Of Metals In Air Borne Particulate Matter (Air Filters) Using Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer

The instrument EDXRF Spectrometer is used to measure the elemental composition of the particles collected on Teflon filters. In EDXRF, X-ray produced by a source irradiates the sample. The elements present in the sample will emit fluorescent X-ray radiation with discrete energies that are characteristic for these elements. By measuring the energies of the radiation emitted by the sample it is determined which elements are present and by measuring the intensities of the emitted energies it is determined how much of element is present in the sample.The air filter application was set up in the instrument according to EPA method IO-3.3. and calibrated with 42 commercially available air filter standards and a blank sample. The standards were composed of pure elements and compounds deposited on 40 mm Nuclepore media. The detection limits for this application were calculated and are based on 3 sigma. The 42 elements that could be measured through EDXRF with its detection limits are given in **Table:27**

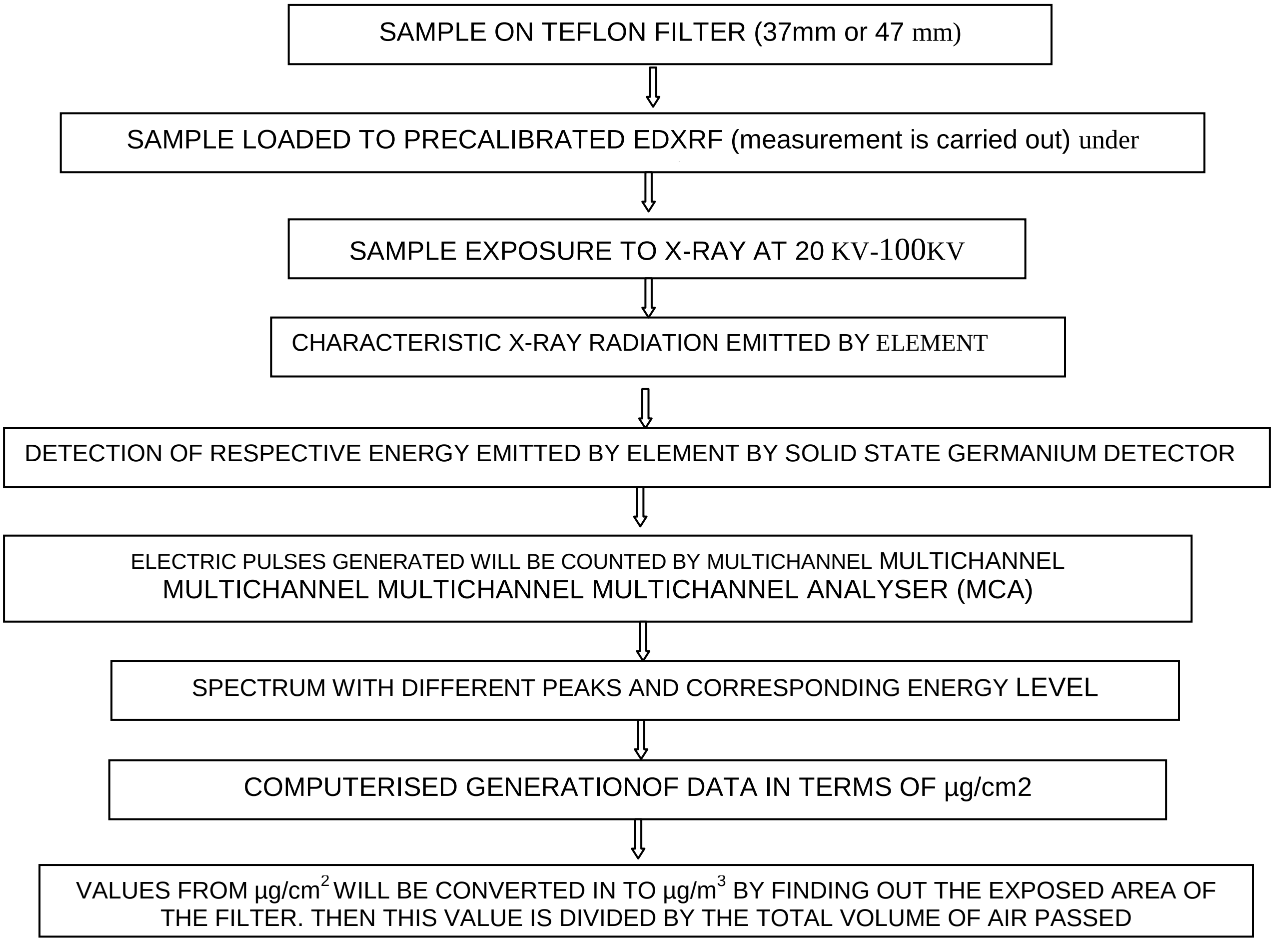
Table 27: List of elements with its detection limits (3 sigma) for particulate matter on air filter using EDXRF

S.No	Name of the element	Symbol	Detection Limit in µg/cm2	S.No	Name of the element	Symbol	Detection Limit in µg/cm2
1	Sodium	Na	3.2599	22	Arsenic	As	0.0012
2	Magnisium	Mg	1.5188	23	Selenium	Se	0.0019
3	Aluminium	Al	0.0824	24	Bromine	Br	0.0048
4	Silicon	Si	0.0509	25	Rubidium	Rb	0.0020
5	Phosphorus	P	0.0068	26	Strontium	Sr	0.0129
6	Sulphur	S	0.0169	27	Yttrium	Y	0.0080
7	Chlorine	Cl	0.0152	28	Molybdenum	Mo	1.0054
8	Potassium	K	0.0048	29	Rhodium	Rh	0.0219
9	Calcium	Ca	0.0037	30	Palladium	Pd	0.0227

S.No	Name of the element	Symbol	Detection Limit in µg/cm2	S.No	Name of the element	Symbol	Detection Limit in µg/cm2
10	Scandium	Sc	0.0031	31	Silver	Ag	0.0170
11	Titanium	Ti	0.0047	32	Cadmium	Cd	0.0258
12	Vanadium	V	0.0014	33	Tin	Sn	0.0223
13	Chromium	Cr	0.0023	34	Antimony	Sb	0.0274
14	Manganese	Mn	0.0048	35	Tellurium	Te	0.0297
15	Iron	Fe	0.0061	36	Iodine	I	0.0161
16	Cobalt	Co	0.0018	37	Cesium	Cs	0.0395
17	Nickel	Ni	0.0022	38	Barium	Ba	0.0362
18	Copper	Cu	0.0034	39	Lanthanum	La	0.0671
19	Zinc	Zn	0.0045	40	Tungsten	W	0.0514
20	Gallium	Ga	0.0134	41	Gold	Au	0.0173
21	Germanium	Ge	0.0083	42	Lead	Pb	0.0054

EDXRF is a non-destructive analytical technique and it requires no sample preparation. The analysis is very fast and accurate.

Flow chart for the analysis process of samples from EDXRF



CHAPTER 13

ASBESTOS

Asbestos is the name given to a number of naturally occurring fibrous silicate minerals that have been mined for their useful properties such as thermal insulation, chemical and thermal stability, and high tensile strength. Asbestos is commonly used as an acoustic insulator, thermal insulation, fire proofing and in other building materials. The three most common types of asbestos are: a) chrysotile, b) amosite and c) crocidolite. Chrysotile, also known as white asbestos is the commonest. Asbestos is made up of microscopic bundles of fibers that may become airborne when distributed. These fibers get into the air and may become inhaled into the lungs, where they may cause significant health problems.

Health effects

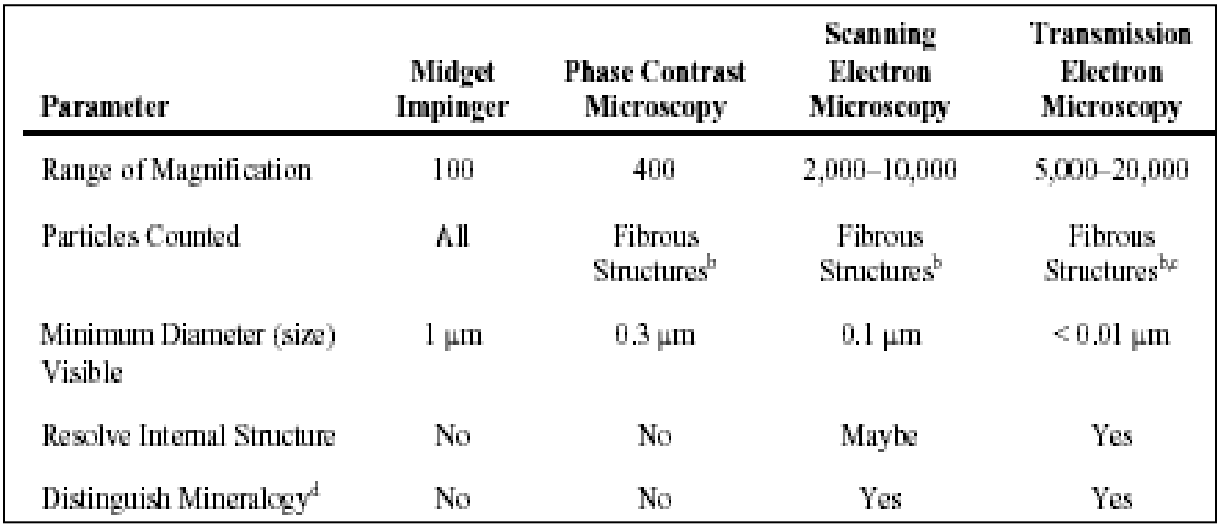
Asbestosis, a lung disease first found in naval shipyard workers., is caused due to exposure to asbestos fibres. As asbestos fibers are inhaled, they may become trapped in the lung tissue. The body tries to dissolve the fibers by producing an acid. This acid, due to the chemical resistance of the fiber, does little to damage the fiber, but may scar the surrounding tissue. Eventually, this scarring may become so severe that the lungs cannot function. The latency period is often 25-40 years.

Another disease, called **Mesothelioma**, a cancer of the pleura (outer lining of the lung & chest cavity) and/ or the peritoneum (lining of the abdominal wall), has been known to occur due to asbestos exposure. The latency period is often 15-30 years. Besides these, **Lung Cancer**, cancer of the **gastrointestinal tract** can also be caused by asbestos. The latency period for cancer is often 15-30 years.

COUNTRY	LEVELS
USA	< 0.2 - 11
South Africa	0.2
Germany	3 - 10
Canada	4 - 9
Austria	0.1 – 4.6

Measurement Method - Four techniques are used to quantify Asbestos, viz. Midget Impinger (MI), Phase Contrast Microscopy (PCM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). MI and PCM are the two analytical techniques used to derive exposure estimates in the majority of epidemiology studies from which the existing risk factors are derived. SEM is an analytical technique that has been employed in several key animal studies. TEM provokes interest because it is the only analytical technique that is potentially capable of distinguishing all of the characteristics of asbestos that potentially affect biological activity.

Table 28 – Analytical techniques used for Asbestos measurement



Parameter	Midget Impinger	Phase Contrast Microscopy	Scanning Electron Microscopy	Transmission Electron Microscopy
Range of Magnification	100	400	2,000–10,000	5,000–20,000
Particles Counted	All	Fibrous Structures[b]	Fibrous Structures[b]	Fibrous Structures[b,c]
Minimum Diameter (size) Visible	1 µm	0.3 µm	0.1 µm	< 0.01 µm
Resolve Internal Structure	No	No	Maybe	Yes
Distinguish Mineralogy[d]	No	No	Yes	Yes

The maximum permissible limit in the air is **0.2 fibers/ cm^3** of air.

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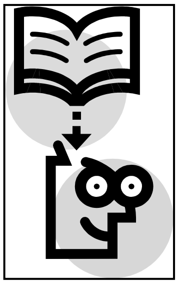
CHAPTER 14

CONTROL MEASURES

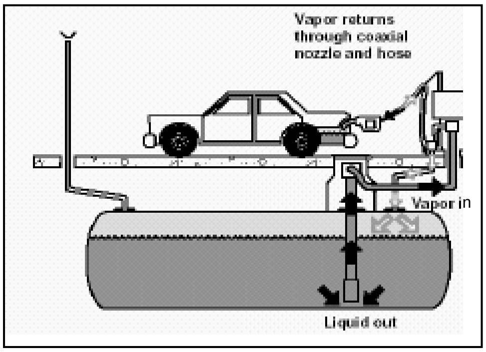


The government has taken a number of measures such as creation and enforcement of legislation, emission standards for industries & vehicles, guidelines for siting of industries, environmental audit, EIA study before setting up or expansion of a project, vehicular pollution control measures, pollution prevention technologies, action plan for problematic areas, development of environmental standards, and promotion of environmental awareness & the role of all stakeholders in pollution control. However, despite all these measures, air pollution still remains one of the major environmental problems.

The EPA has established standard permissible limits for the maximum levels of toxic air pollutants that can be emitted by some major industrial sources, such as chemical plants, oil refineries, aerospace manufacturers, and steel mills, as well as categories of smaller sources, such as dry cleaners, commercial sterilizers, secondary lead smelters, and chromium electroplating facilities.

Following are a few recommendations for sustainable environmental management:

1. Appropriate enforcement of laws to facilitate compliance with vehicular and industrial emission standards (EURO II norms for vehicles throughout the country from 2005 and banning of 15 years old commercial vehicles)
2. Adoption of cleaner and environment friendly fuels (like CNG in Delhi). Some examples are fuel cells for vehicles, Liquified Natural Gas (LNG), battery driven vehicles etc
3. Continual improvement in the existing fuel quality (e.g. introduction of unleaded petrol, low sulphur diesel). There is a need, in India, to enforce laws related to improved fuel quality especially for vehicles.
4. Improved engine design that is environment friendly (e.g., Introduction of 4-stroke two wheelers)
5. Regular ambient and source air quality monitoring and surveillance including the pollutant emission levels of vehicles
6. The industries using hydrocarbons should be prompted to recover the evaporative emissions these for further use. Such industries include dry cleaning operations, Printing and publishing, petrol distribution, Surface coating (metal can, wire, furniture etc.) etc.
7. The reduction in evaporative hydrocarbons from consumer products can be achieved only by replacing the commonly used solvents by less volatile solvents. Paints, varnishes, sprays, printing inks, aerosols are some of the products for which solvent replacement can be considered e.g., Indian paint industry is focusing its R&D on water based paints.



Fuel Recovery during refueling

8. Putting up a ban on activities like open burning of refuse (instead compost the waste)

9. Creating mass awareness and training people on ways to reduce their usage of consumer goods like air fresheners, hair sprays, deodorants, nail polish remover, shaving creams, etc.
10. Establishing more means of mass transit system (public vehicles) and promoting their use (e.g., metro rail in Delhi) and also promoting car pooling
11. Recognizing and rewarding community groups working towards air pollution prevention and control

Box 10 - DRY CLEANING

The primary emission is the solvent. In dry cleaning units using petroleum, solvent recovery is not recommended due to fire hazards associated with collecting the vapours. However, some emissions control can be obtained by adopting good operating practices and maintenance of equipments (e.g. Prevent link accumulation, solvent leakage etc.) Adsorption on carbon cartridges and incineration are technically feasible however, incur high costs. For perchloroethylene using dry cleaning units' solvent recovery is recommended. Recovery is affected on the washer, dryer, still and muck cooker by using condensers, water /solvent separators and carbon adsorption units. Solvent in carbon adsorption unit is desorbed with steam, condensed and separated from the condensed water and returned to pure solvent storage tank.

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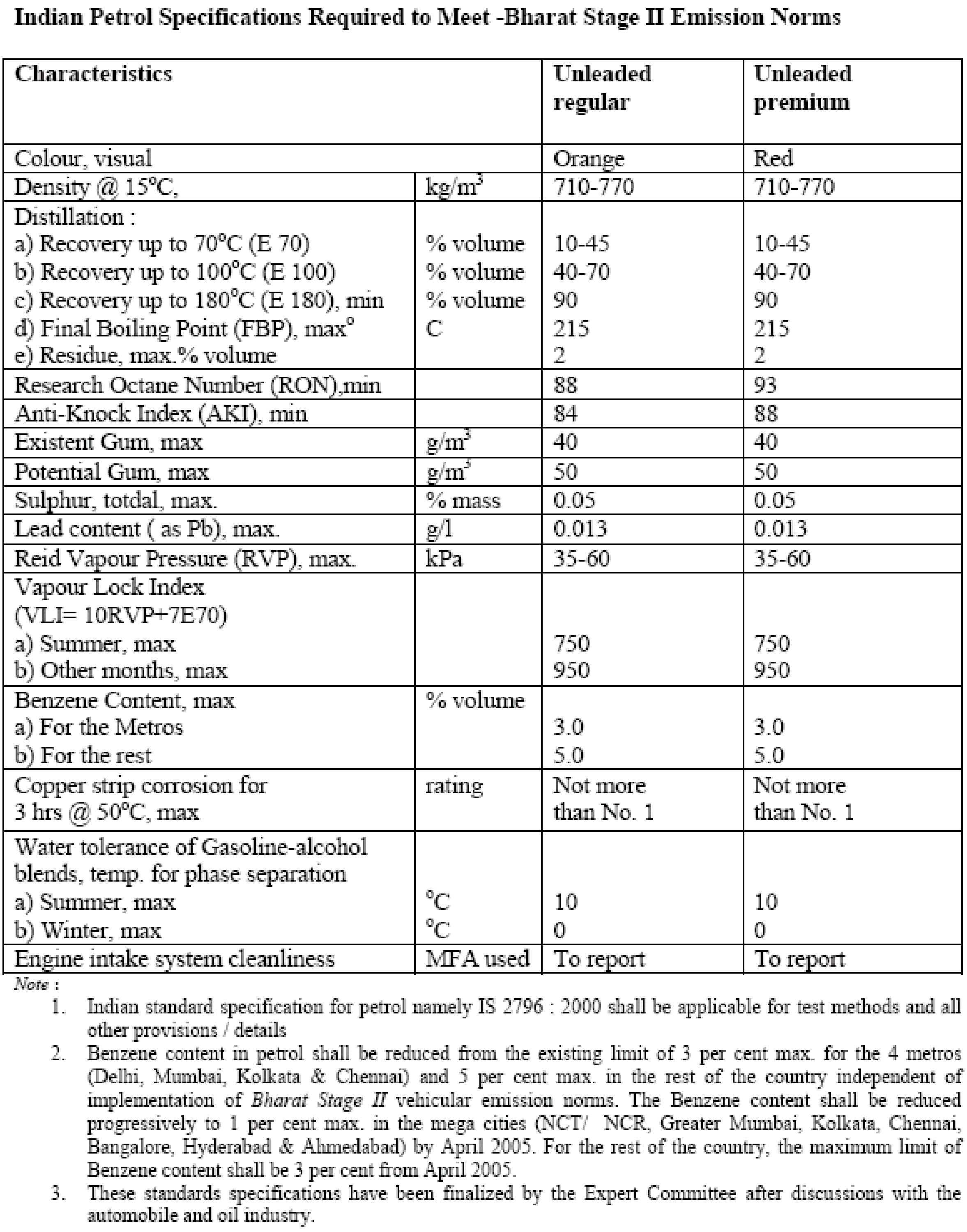

Indian Petrol Specifications Required to Meet -Bharat Stage II Emission Norms

Characteristics		Unleaded regular	Unleaded premium
Colour, visual		Orange	Red
Density @ 15°C,	kg/m^3	710-770	710-770
Distillation :			
a) Recovery up to 70°C (E 70)	% volume	10-45	10-45
b) Recovery up to 100°C (E 100)	% volume	40-70	40-70
c) Recovery up to 180°C (E 180), min	% volume	90	90
d) Final Boiling Point (FBP), max°	C	215	215
e) Residue, max.% volume		2	2
Research Octane Number (RON),min		88	93
Anti-Knock Index (AKI), min		84	88
Existent Gum, max	g/m^3	40	40
Potential Gum, max	g/m^3	50	50
Sulphur, totdal, max.	% mass	0.05	0.05
Lead content (as Pb), max.	g/l	0.013	0.013
Reid Vapour Pressure (RVP), max.	kPa	35-60	35-60
Vapour Lock Index (VLI= 10RVP+7E70)			
a) Summer, max		750	750
b) Other months, max		950	950
Benzene Content, max	% volume		
a) For the Metros		3.0	3.0
b) For the rest		5.0	5.0
Copper strip corrosion for 3 hrs @ 50°C, max	rating	Not more than No. 1	Not more than No. 1
Water tolerance of Gasoline-alcohol blends, temp. for phase separation			
a) Summer, max	°C	10	10
b) Winter, max	°C	0	0
Engine intake system cleanliness	MFA used	To report	To report

Note :

1. Indian standard specification for petrol namely IS 2796 : 2000 shall be applicable for test methods and all other provisions / details
2. Benzene content in petrol shall be reduced from the existing limit of 3 per cent max. for the 4 metros (Delhi, Mumbai, Kolkata & Chennai) and 5 per cent max. in the rest of the country independent of implementation of *Bharat Stage II* vehicular emission norms. The Benzene content shall be reduced progressively to 1 per cent max. in the mega cities (NCT/ NCR, Greater Mumbai, Kolkata, Chennai, Bangalore, Hyderabad & Ahmedabad) by April 2005. For the rest of the country, the maximum limit of Benzene content shall be 3 per cent from April 2005.
3. These standards specifications have been finalized by the Expert Committee after discussions with the automobile and oil industry.

High Speed Diesel / Gas Oil

IS 1460 : 1995 (Amendment No. 2, March 1999 & No. 3, March 2000) Table 1: Requirements for Diesel Fuels (Clause 4.2)

Sl No.	**Characteristics**	**Requirements**		**Method of Test Ref to [P:] of IS 1448**	
		HSD	**LDO**	**Annex**	
(1)	(2)	(3)	(4)	(5)	(6)
	Carbon residue (Ramsbottom) on 10 percent residue, percent by mass, Max	0.30	1.5 (on whole sample)		P : 8
	Total sulphur, percent by mass, Max	0.25	1.8		P: 33
	Total sediments, mg per 100 ml, Max	1.6		A	

Total sulphur content for HSD shall stand automatically revised as per the following schedule; although efforts will be made by the oil companies to reduce sulphur content below 1.0 percent by mass even before 1998:

	1998	2000
Total sulphur content, percent by mass, max	0.50	0.25

Proposed Minimal National Standards (MINAS) for discharge of toxic effluents from Petroleum Oil refineries

S.No	Parameter	Limiting value for concentration (mg/l)	Limiting value for quantum (kg/1000 tonne of crude processed)	Averaging Period
Parameters to monitored once in a month: grab samples for each shift with 8-hours' interval				
1.	Benzene	0.1	0.04	Grab
2.	Benzo(a) pyrene	0.2	0.08	-do-
3.	Phenols	0.35	0.14	-do-
Parameters to monitored once in a month: composite sample (with 8-hours' interval) for 24-hours flow weighted average				
4.	Ni	1.0	0.4	24-hours
5.	Pb	0.1	0.04	-do-
6.	V	0.2	0.8	-do-

S. No.	Parameter	Existing refineries	New refineries or FCC, furnaces, boilers commissioned after January 01, 2006
1.	Ni + V from furnace and boilers	5	5
2.	Ni + V from FCC regenerators	5	2

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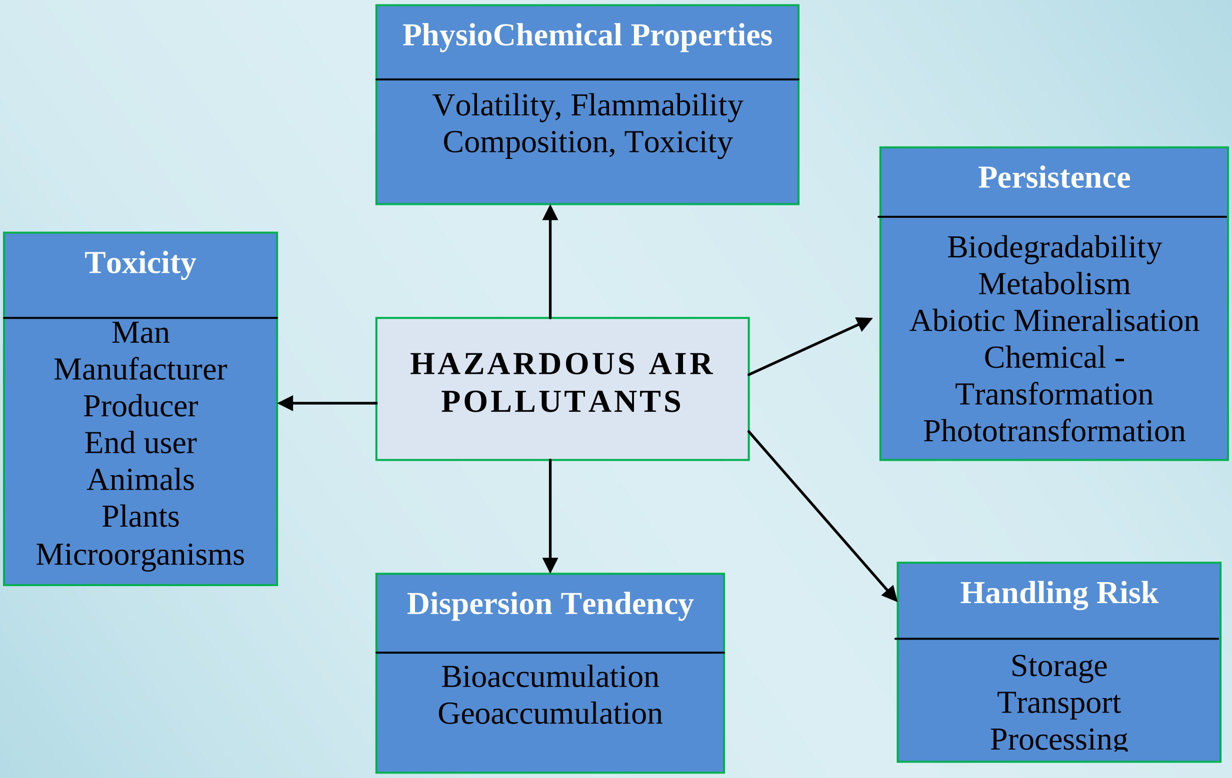

HAZARDOUS AIR POLLUTANTS

PhysioChemical Properties

Volatility, Flammability
Composition, Toxicity

Toxicity

Man
Manufacturer
Producer
End user
Animals
Plants
Microorganisms

Persistence

Biodegradability
Metabolism
Abiotic Mineralisation
Chemical -
Transformation
Phototransformation

Dispersion Tendency

Bioaccumulation
Geoaccumulation

Handling Risk

Storage
Transport
Processing

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