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Polynuclear Aromatic Hydrocarbons (PNHS)- Toxic Air Pollutants (TAPS): A Review

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Abstract

In the environment by various processes such as incomplete combustion of recent and fossil organic matter at higher temperatures, slow maturation of organic matter under geochemical gradient conditions. Most PNH inputs in the environment are linked to the anthropogenic activity that is generally considered to be the major source of these compounds.

PNHs have different distribution patterns according to their production sources. In addition, physical–chemical properties of some PNHs, like chemical reactivity, can contribute to modify the original distribution pattern of the emission sources. PNHs in general are toxic, carcinogenic in many animals, act as anti-estrogens in mammals, and induce reproductive toxicity in women. Degradation is the most common way to remove PNHs in the environment. PNHs partially dissolved in water tend to be adsorbed in suspended solids PNHs in water bodies can accumulate in fatty tissues of organisms through the food chain. Thus, it is imperative to understand the relative importance of pollutant emission sources for coastal air and watersheds.

Keywords: PNHS; Taps; Cops; Toxic; Carcinogenic.

Toxic Air Pollutants

Toxic air pollutants are known or suspected to cause cancer or other serious health effects, which is found in gasoline; perchlorethylene, which is emitted from some dry cleaning facilities and methylene chloride, which is used as a solvent and paint stripper by a number of industries. Other listed air toxics include polycyclic aromatic hydrocarbons.

Environmental Protection Agency (USA) identifies a list of the 33 air toxics that present the greatest threat to public health in the largest number of urban areas. Of these 33 urban air toxics, EPA has identified the 30 with the greatest contribution from smaller commercial and industrial operations or so-called "area" sources.

Principal Pollutants and Air Toxics

Air pollutants can be divided into two categories: principal pollutants and air toxics. Principal pollutants are often considered a group of 'traditional' air pollutants. These have a demonstrable health toxic. The principal pollutants constitute mainly carbon monoxide, sulphur dioxide, photochemical oxidants (as ozone), oxides of nitrogen, lead and particles. Air toxics are pollutants present in the environment in low concentration (other than principal pollutants) that are known, or suspected to be as toxic and persistent. The term 'air toxics' and 'toxic air pollutants' (TAP) are used interchangeably. Some PNHs are semi volatile in nature & therefore, these can be present in particulate as well as vapour phase while others are mostly adsorbed onto particles in the environment (IARC, 1983).

Conscious Organic Pollutants (COPs)

Conscious organic pollutants (COPs) are amongst the most dangerous substances released by humans into the environment. COPs include a wide range of substances, including organochlorine conscious. They possess toxic characteristics and are likely to causesignificant adverse effects on health of exposed wildlife and humans, such as allergy, damaged nervous system and immunity, congenital diseases, cancer. These substances are conscious, resist degradation under natural conditions and remain unchanged in the environment for a long period. The upper tropic levels of food chains (fish, predatory birds, mammals and humans) can bio accumulate the highest concentrations of COPs. Very often the alternatives to conscious organic pollutants are available. But the high costs, poor public awareness, lack of appropriate infrastructure and technologies are the reasons why these alternatives are not being used widely enough.

Possible solutions to these problems should be adjusted to the properties and possible use of each substance, as well as to the climatic and socio-economic circumstances of each country (AMAP, 2002).

Polynuclear Aromatic Hydro-Carbons (PNHs)

Chemicals can be transported through the environment by several mechanisms. Even pristine areas are subjected to the deposition of chemicals carried thousands of kilometres through the atmosphere. Polynuclear Aromatic Hydrocarbons (PNHs) are chemicals containing two or more fused benzene rings in a linear, angular or cluster arrangement (Masih and Taneja, 2006). PNH contain only carbon and hydrogen. They belong to the group – Conscious Organic Pollutants (COPs) known for their chemical Carcinogenicity (EPA, 1986; Masih et al, 2008). They are members of a unique class of air pollutants relevant to many scientific and societal issues having a variety of aspects: chemical, toxicological, engineering, technological, public health, economic, regulatory and legislative (Pitts & Pitts, 1996). PNHs are released into ambient air as constitutes of highly complex mixtures of Polynuclear Organic Matter (POM). As defined in the U.S. Clean Air Act Amendments of 1990 (CAAA, 1990), POM "includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 212oF (100°C)". The ubiquitous nature of these airborne PNHs is evident from the fact that the 16 U.S. Environmental Protection

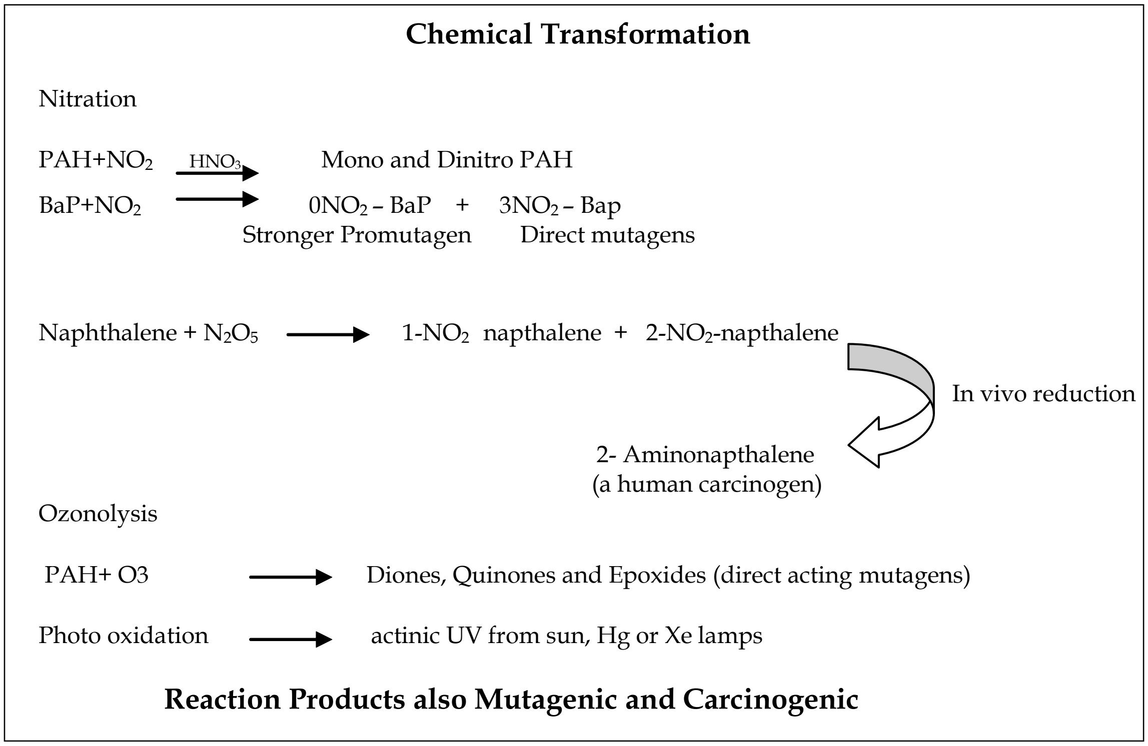

Fig. 1: Reaction of PNHs with atmospheric pollutants viz. NO2& O3

Agency "Priority Polynuclear Aromatic Hydrocarbons Pollutants" shown in Table 1 are found in urban air sheds throughout the world (U.S.EPA, 1988). Polynuclear aromatic hydrocarbons (PNH's) are an important group of compounds which are transported through the atmosphere. Their widespread presence is due to their emissions from a wide range of combustion sources, including diesel and gasoline engines, biomass burning of agricultural and forest fuels (Jenkins et al 1996; Masih et al, 2010), and outdoor wood smoke (Schauer et al, 1999). PNHs are also common constituents of air indoors, arising from coal and wood combustion (Mumford et al, 1990) and environmental tobacco smoke, ETS (California EPA, 1997).

Formation of PNHs

PNH are usually generated under insufficient combustion (pyrolysis) conditions, such as insufficient oxygen (Sorensen, 1994; Nam et al, 2003) or high temperature pyrolytic process during combustion of fossil fuels/ organic materials, as well as in natural processes such as carbonization(pyro synthesis). Thus, PNHs are the constituents of the products of incomplete combustion (PIC). PNHs on reaction with atmospheric pollutants viz., NOx, SO2, O3 etc. may form hetro-PNHs. The products formed during the chemical transformation (Figure 1) are more mutagenic and carcinogenic than the parent compounds. The contribution from natural sources of PNHs is limited, being restricted to spontaneous forest burning and volcanic emissions (Bourotte et al, 2005).

Vapour Particle Phase Distrbution of PNHS

According to review and analysis done by white et al, (1980) PNHs and nitro-PNHs may exist in vapour or particle phase .The lower molecular weight PNHs and nitro-PNHs with a ring number of 2and 3 tend to be associated with the vapour phase. The larger molecular weight PANs tend to be associated with particulate in the atmosphere. PNHs species with a molecular weight below that of pyrene exist to a larger extent in the gas phase. On an average 47% of the total PNH were reported in gas phase. Three ring PAN are predominantly gaseous, four ring PNH mixture of both phases and five-six ring PHN primarily particulate. Pierce and Katz (1975) also studied size distribution of PHN containing particulates, which showed approximately a log-normal relationship for suburban and rural sampling sites with majority of PNH content (50-78%) associated with particles below 3.0 μm diameter. Total PNHs were higher period by a factor of 65-75% and concentration range vary between lowest 2 μg gparticulate (anthracene) to 20 μg/g (BghiP).

Air-Soil Exchange/Interaction of PNHS

Polynuclear aromatic hydrocarbons are often found in air, precipitation, lakes, estuaries, soil, sediments and groundwater systems. Once released into the atmosphere PNHs are highly persistent in the environment and migrate within and between the atmosphere, terrestrial and aquatic compartments. Atmospheric deposition constitutes the main input of semi-volatile organic compounds to soil (Tremolada et al., 1996). Once entered in the soil they accumulate in horizons rich in organic matter where they are likely to be retained for many years due to their persistence and hydrophobicity. (Krauss et al., 2000). Soil is the primary terrestrial reservoir of persistent organic pollutants such as PANs (Ribes et al., 2002; Wileke et al., 1996) and the atmosphere is their main transport vector (Drooge, 2002), so, it is important to determine the amounts of PNHs in soil as their concentration in soil correlates significantly with the corresponding levels in air (Nam et al, 2003; Massei et al, 2004) and is a good indicator of the surrounding air pollution and the proximity of sources. Soil air exchange is therefore a key process governing the environmental fate of these compounds on a regional and global scale. Air to soil transport may occur through dry depositions of aerosols, wet deposition or sorption to soil constituents (Cousins, 1999). Soil to air diffusion is

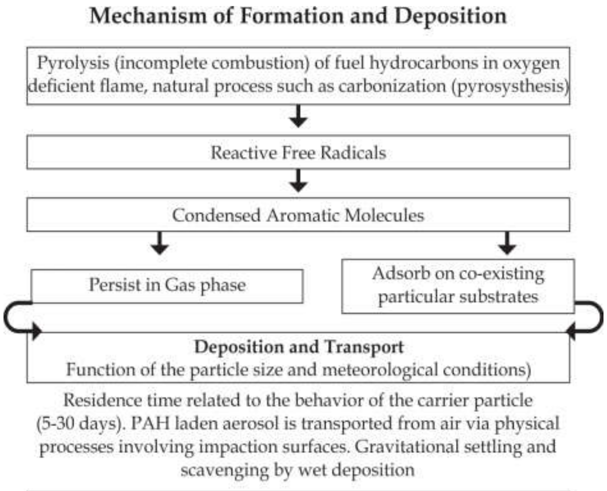

Fig. 2: Mechanism of Formation & Deposition of PNHs.

driven by the chemical potential gradient between the soil and the atmosphere (Masih et al, 2012). Consequently, soils are an important reservoir for these compounds (Ockenden et al., 2003) andexchanges between soils, water and the atmosphere is a widely studied process (Bidleman and McConnell,1995; Wania and Mackay, 1996).

Structure of PNHs

In general, hydrocarbons that display benzene like properties are called aromatic; those which contain fused benzene rings are called polynuclear or (polynuclear) aromatic hydrocarbons or PNHs for short. Like benzene itself many PNHs possess unusually great stability and a planar geometry (Colin Baird, 1999). There is a series of benzene like hydrocarbons that contains several six membered rings connected together by the sharing of a pair of adjacent carbon atoms between adjoining fused rings. The simplest example is naphthalene C10H8 as shown in Figure. Notice that there are ten, not twelve, carbon atoms in total and that there are only eight hydrogen atoms, since the shared carbons have no attached hydrogen's. As compound naphthalene is a volatile solid whose vapour is toxic to some insects. It has found use as one form of "moth balls", the other being 1, 4-dicholorobenzene. Other than naphthalene, PHNs are not manufactured commercially, since they have no uses. Conceptually, there are two ways to fuse a third benzene ring to two carbons in naphthalene, one result in a "linear" arrangement for the centers ('the nuclei') of the rings while the other is a "branched" arrangement (Figure 2). Both anthracene and phenanthrene are pollutants associated with incomplete combustion, especially of wood and coal, and are also released in to the environment from the dump sites of industrial plants that converts coal into gaseous fuel, and fro petroleum and refineries. In rivers and lakes, they are found mainly attached to sediments rather than dissolved in the water, both are found to be subsequently partially incorporated by fresh water mussels (Masih et al, 2014).

Sources of PNHs

Individual sources of PNHs are characterized by combustion processes with PNH-containing compounds, e.g. processing of coal, crude oil, creosote, coal-tar, bitumen and vehicular exhausts (Gasoline and Diesel). The sources considered are industrial, domestic, mobile, agricultural and natural (PNH Position Paper, 2001).

Industrial Sources

In general industrial sources are comparatively well understood and are increasingly being regulated. Currently these include: Petrochemical and related industries, cement manufacture, rubber tyre manufacturing, bitumen and asphalt industries, commercial heat and power, waste incineration, creosote and wood preservation, coke production. Overall PNH emissions are believed to be decreasing; improved energy management is leading to improved combustion which, in turn, leads to lower emissions.

Domestic Sources

The domestic sources of PNH which can influence ambient air quality are:

Cooking, use of diesel generators, incineration, smoking cigarettes, cigar and tobacco. The usage of heavy diesel generators to generate electricity because of erratic electricity supply is predominant. Modern gas and oil burners used for cooking have relatively low PNH emissions.

Mobile Sources

Mobile sources are modes of transport reliant on a combustion engine. This includes aircraft, shipping, railways, automobiles and motor vehicles including off-road vehicles and machinery. Automobile internal combustion engines are generally fuelled by gasoline (petrol) or diesel fuels. There are a relatively small proportion of vehicles which run on LPG or LNG. Two-Stroke engines are relevant in the motor scooter and motor cycle sector of transportation. Two-stroke fuel is a mixture of gasoline and oil. The engines are generally small and not equipped with additional emission control systems. Recent search has estimated that unabated PANemission whilst performing the ECE R40 simulation are 1.6 mg km-1 for the sum of 29 PANs with 2 to 6 rings and 20.8 µg kg-1 for six carcinogenic PNHs (BaP, B[b+k]F, BaA, DBahA). One of the major influences on the production of PNH from gasoline automobiles is the air-to-fuel ratio; it has been found that the amount of PNH in engine exhausts decreases with a leaner (thin) mixture. The use of catalytic converters has also been shown to have a significant effect on the reduction of the PNH concentration in the exhaust gases. All internal combustion engines have varying PNH emission characteristics dependent on engine temperature (particularly cold-start), load, fuel quality and speed. Urban areas with congested traffic conditions and with vehicles often only traveling short journeys promote the emission of PNH. Engine deterioration and high mileage also increases emissions. Studies have shown that for all PNH compounds studied the reduction achieved due to catalytic converters was between 80 and 90% (for BaP 94%). Catalytic converters for diesel engines also reduce total PNH emissions, however the reductions are not as high as for gasoline engines. Diesel fuelled vehicles have higher particulate emissions than gasoline fuelled vehicles. The particles consist of combustion-generated soot, a solvent extractable hydrocarbon fraction. Other control technologies are currently being developed and improved (trap oxidizers and filters for example) for heavy-duty diesel engines. Such devices will be necessary to meet emission limit values set within EU regulations ('EURO 4'). As for gasoline vehicles, an additional source of PNH in the exhaust of diesel fuelled vehicles is the PNH content in the fuel i.e. by reducing fuel PNH content a reduction of exhaust PNH can be achieved. The popularity of the diesel engine in heavy-duty applications in trucking, railroad, marinetransport, DG sets and construction industry is due to both its fuel efficiency and long service life relative to the gasoline engine. Compared with gasoline engine, diesel emissions are lower in carbon monoxide (CO), hydrocarbon (HC), and carbon dioxide (CO_2), but higher in oxides of nitrogen (NOx) and particulate matter (PM). Diesel exhaust is a complex mixture of both particulate and gaseous phase. Diesel exhaust has particulate with mass median diameter of 0.05 to 1.00 micrometer, a size rendering them easily respirable and capable of depositing in the airways and alveoli. The particles consist of a carbonaceous core with a large surface area to which various hydrocarbons are absorbed, including carcinogenic poly nuclear aromatic hydrocarbons [Benzo(a)Pyrene] and Nitro-PNHs that have elicited the most concern with respect to human health. If only the most harmful of the exhaust emissions that is particulate emission is considered, the carcinogenic effect of one new diesel car is equivalent to 24 petrol cars and 84 new CNG cars on the road. The honorable Supreme Court of India has restricted the use of commercial diesel driven vehicles in Delhi due to its harmful effects (CPCB, 2003). The main source of PNH emissions in rail transport is the use of diesel and diesel-electric locomotives. As some locomotives are old, and produce large amount of black smoke, they may be a significant source of PNH but no measurement data are available. There have been very few studies carried out on PNH emissions of aircraft, and of those carried out, most have been for military aircraft. However, the results show that PNH emissions are dependent on fuel composition (volatility). Average emission factors for an aircraft gas turbine engine have been given as 1.24 mg/LTO (Landing-Take Off cycle) for BaP. As air travel increases the proportion of total PNH emissions, which are attributable to, air transport could increase, though it is unlikely that it will become a major contributor to total PNH emissions. Particulate emissions from shipping are not currently regulated. There are a limited number of publications focusing on PNH emissions from shipping. PNH emissions from an onboard marine diesel engine (6600 kW, maximum continuous rating) burning marine diesel fuel with a Sulphur content of 1.9% (w/w). Within the Lloyds Marine Exhaust Emissions Research Programme, individual PNH from several different ships using marine distillates and heavy bunkers were measured.

Agricultural Sources

Activities like stubble burning, openburning of moorland heather for regenerationpurposes, open burning of brushwood, strawand use of diesel generators for irrigationpurposes, involve the burning of organicmaterials under sub-optimum combustionconditions. Thus it can be expected that a significant amount of PNH are produced. Insome countries there are regulations in placeregulating these activities. Due touncertainties in emission factors and theoccurrence of these activities, the emissions of PNH from agricultural sources are difficult toquantify. Nevertheless, they may contributesignificantly to PNH level at certain locations.

Natural SourcesNatural sources of PNH include theaccidental burning of forests, woodland,moorland etc. Meteorological conditions (suchas wind, temperature, humidity) and fuel type(moisture content, green vs. seasoned wood,etc.) may play an important role in the degreeof PNH production. Another natural source ofPNH are volcanic eruptions. No data are available regarding these emissions and theircontribution to the overall PNH profile.

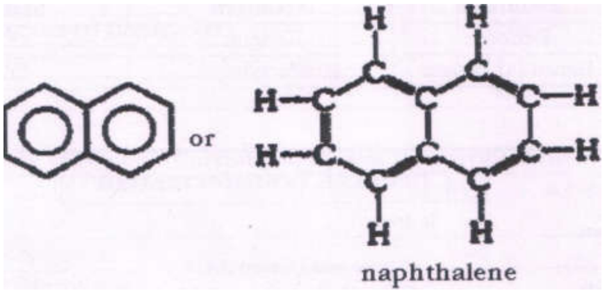

Fig. 3: Structure of Naphthalene

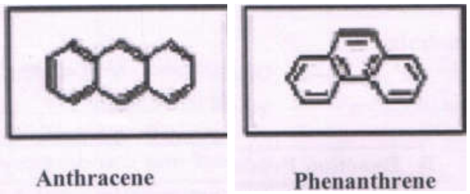

Fig. 4: Linear & Branched Arrangement of Benzene Molecule Selected PNHs

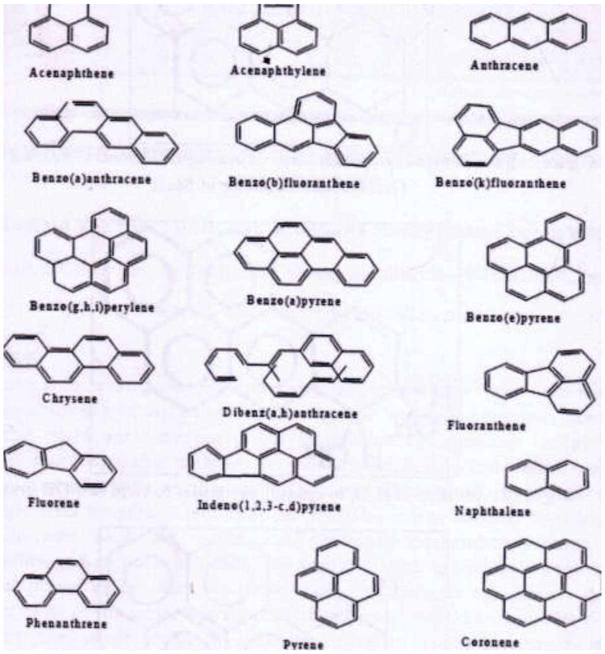

Fig. 5: Structure of selected PNHs

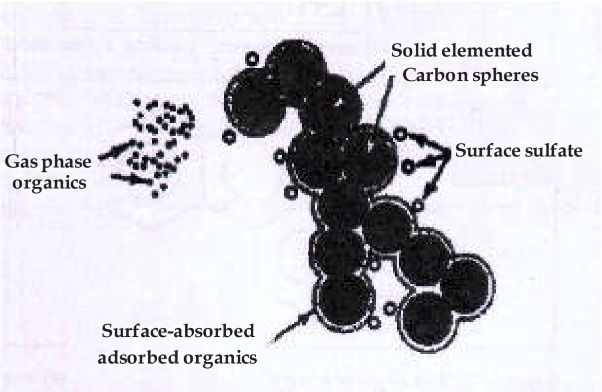

Fig. 6: Physio-chemical Complexity of Primary Combustion-generated POM

Oxy-PNHs

Oxy-PNHs are semi-volatile compounds, with high molecular weights and lower vapour pressures than their parent PNHs. Their sources can be both natural and anthropogenic. These compounds also could be originated from reactions between PNHs and other compounds founded in ambient air. Allen et al. (1997) mentioned that these compounds could originate from phoNto-oxidation of PNHs. There are experiments which suggest that several of the PNHs that are emitted in sizable amounts from various natural and anthropogenic sources are degraded in the atmosphere by sunlight or by interactions with other reactive airborne species as O_3, NO_x, and from these reactions products founded were quinones, ketones, coumarines, aldehydes and acids (Pitts et al., 1980). Oxy-PNHs may befounded in gas phase or may be adsorbed onto particles (Pankow et al., 1993). Pierce and Katz (1975), investigated that benzanthrone and phenalen-1-one concentrations increased in respirable particulate matter during winter. Oxy-PNHs were founded to be mutagenic in bacterial and human cell mutation assays (McDonald et al., 2004). PNHs are oxidized into oxygenated derivatives (Oxy-PNHs) by UV-light, O_3, NO_x and reactiveoxygen species. There are studies which show us that particulate matter emitted from vehicles contain higher amounts of Oxy-PNHs than particulate matter found in the atmospheric air (Oda et al., 1998).

Physio-Chemical Properties of PNHs

PNHs are Colourless, white or pale yellow-green solids. They are planar, relatively inert and volatile in nature. Their Melting Point is generally at room temperature while their Boiling Point is above than 100^{o}C. The physical and chemical complexity of primary combustion-generated POM is illustrated in Figure 3 (Johnson et al, 1994), a schematic diagram of a diesel exhaust particle and associated co-pollutants. The gas-phase regime contains volatile (2-ring) PNHs and a fraction of the semivolatile (3- and 4-ring) PNHs. The particle phase contains the remainder of the semivolatile PNHs (particle associated) along with the 5- and 6-ring heavy PNHs adsorbed/absorbed to the surface of the elemental carbon spheres that constitute the backbone of overall diesel soot particles. PAHs have low solubilities in water as expected from their non-polar character. These decrease dramatically in going from the 2- and 3- ring compounds (e.g., naphthalene, with a solubility of 31 mg L-1) N0.26 mgL-1) to 5-ring B(a)P, with a solubility of only 0.0038 mgL-1) (Mackay et al, 1992). However reactions of PNHs in ambient air to form more polar species (e.g., nitro-PAHs, ketones, quinones, lactones and dicarboxylic acids) greatly enhance their solubilities in aqueous systems. This has major implications when one considers the distribution of PAHs and their atmospherically formed PAC derivatives, through air, water and soil environments. These increases in solubility upon

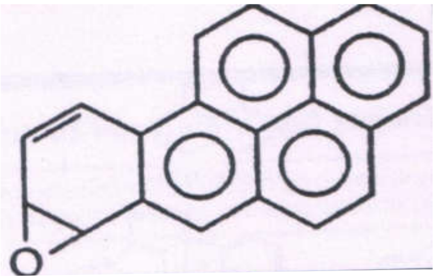

Fig. 7: Formation of an epoxide ring one C=C bond of interest to the Carcinogenic behaviour of B(a)P

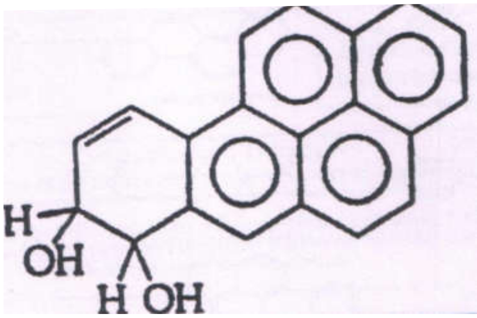

Fig. 8: Addition of H_2O, to epoxide molecule to yield two-OH groups.

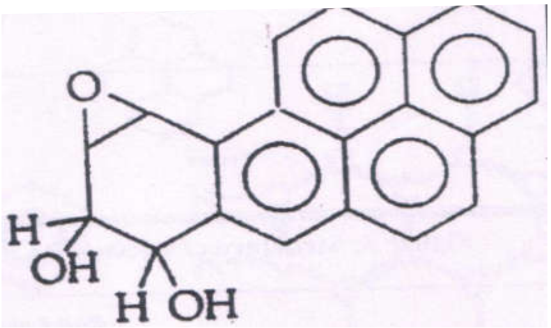

Fig. 9: Epoxidation of two-OH groups

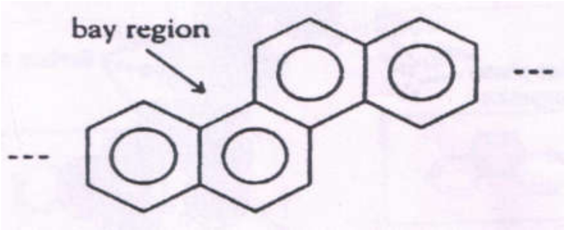

Fig. 10: The Organisation of carbon atoms at a bay region.

reaction are important not only from an environmental chemistry perspective but also in terms of possible impacts on public health and ecosystems, e.g., in both the exposure and the health effect portions of risk assessments of PNHs.

Uses of PNHs

There is no known use for acenaphthylene, benz[a]anthracene, benzo[b] fluoranthene, benzo[e]pyrene, benzo[j] fluoranthene, benzo[k] fluoranthene, benzo[g,h,i] perylene, benzo[a]pyrene, chrysene, dibenz [a,h]anthracene, indeno [1,2,3-c,d] pyrene, or pyrene except as research chemicals (Holloway 1987; HSDB 1994). Anthracene is used as an intermediate in dye production, in the manufacture of synthetic fibre, and as a diluent for wood preservatives. It is also used in smoke screens, as scintillation counter crystals, and in organic semiconductor research (Holloway 1987). Anthracene is used to synthesize the chemotherapeutic agent, Amsacrine (Wadler et al. 1986). Acenaphthene is used as a dye intermediate, in the manufacture of pharmaceuticals and plastics,

Table 1: Common Names, Empirical Formulas, Molecular Weights, Melting Points, Boiling Points, and CAS Numbers for 16 EPA "Priority PAH Pollutants"^{a,b}

Common Names	MW(g mol^{-1})	Empirical Formula	Mp(^{o}C)	Bp (^{o}C)	CAS Number
Naphthalene	128	$C_{10}H_8$	80.5	218	91-20-3
Acenaphthylene	152	$C_{12}H_8$	92	265-275	208-96-8
Acenaphthene	154	$C_{12}H_{10}$	96.2	277.5	83-32-9
Fluorene	166	$C_{13}H_{10}$	116	295	86-73-7
Anthracene	178	$C_{14}H_{10}$	216.2	340	120-12-7
Phenanthrene	178	$C_{14}H_{10}$	101	339	85-01-8
Fluoranthene	202	$C_{16}H_{10}$	111	375	206-44-0
Pyrene	202	$C_{16}H_{10}$	156	360	129-00-0
Benz(a)anthracence	228	$C_{18}H_{12}$	160	435	56-55-3
Chrysene	228	$C_{10}H_{12}$	255	448	218-01-9
Benz(b)fluoranthene	252	$C_{10}H_{12}$	168	481	205-99-2
Benz(k)fluoranthene	252	$C_{10}H_{12}$	217	481	207-08-9
Benzo(a)pyrene	252	$C_{10}H_{12}$	175	495	50-32-8
Benzo(ghi)perylene	276	$C_{10}H_{12}$	277	525	191-24-2
Indeno(1,2,3-cd)pyrene	276	$C_{10}H_{12}$	163	---	193-39-5
Dibenz(a,h)anthenracene		$C_{10}H_{14}$	267	524	53-70-3

Adapted from MacKay et al, (1992); data on Indeno(1,2,3-cd)pyrene from Harvey (1997). Structures and their numbering are based on IUPAC recommendations as described by Loening et al. (1990).b USEPA (1998) designation.

Table 2: Half Lives of PNH under Simulated Atmosphere Conditions (Hrs)

PNH	Simulated Sunlight	Simulated Sunlight+Ozone(0.2ppm)	Dark reaction Ozone (0.2ppm)
Anthenracene	0.20	0.15	1.23
Benzo(a) Anthenracene	4.20	1.35	2.88
Dibenz(a,h)anthenracene	9.60	4.80	2.71
Pyrene	4.20	2.75	15.72
Benzo(a)pyrene	5.30	0.58	0.62
Benzo(a)pyrene	21.10	5.38	7.60
Benzo(b)fluoranthene	8.70	4.20	52.70
Benzo(b)fluoranthene	14.10	3.90	34.90

source: Katz,et al, 1979

Table 3: Intake of Potential Carcinogenic PNHs by non smoker & smokers

Source of PNH	Intake			
	Non-Smoker		Smoker	
	UG day^{-} I	Total %	U day^{-} I	Toyal %
Food	3	9.3	3	44.5
Air	0.16	4.9	0.16	2.4
Water	0.006	0.2	0.006	0.01
Soil(accidental Ingestion)	0.06	1.9	0.06	1.0
Cigrette	-	-	3.5	52
Total	3.22	100	6.72	100

Table 4: Potential Carcinogenicity and Bioactivity of the PNH

S. No.	PNH	Cracinogenicity	Bioactivity
1	Anthenracene	0	0
2	Fluoranthene	0	CC
3	Pyrene	0	
4	Benzo(a)pyrene	+	TI
5	Chrysene	+	Ti
6	Benzo(b)fluoranthene	++	C,TI
7	Benzo(k)fluoranthene	0	0
8	Benzo(a)pyrene	+++	C,TI
9	Dibenz(a,h)anthenracene	+++	C,TI
10	Benzo(ghi)pyrene	0	CC
11	Indeno(1,2,3-cd)Pyrene	+	TI

Note: + to +++ Active, CC= Carcinogen with BaP, TI= Tumour initiator, C= Complete Carcinogen, 0= Inactive

Table 5: Portion of carcinogenicity effect of BaP

Source of BAP	Carcinogenicity of BAP Portion (%)
Automobile exhaust condensate(Gasoline engines)	9.6
Automobile exhaust condensate(Diesel engines)	16.7
Domestic hard coal heating^{a}	6
Domestic brown coal heating (briquets)	9
Lubricating oil of cars (used)	18
Sewage sludge (extracted)	22.9
Cigarette smoke condensate	1

(Source: A. Bjorseth, 1979)

Table 6: Prescribed Ambient Air Quality Guidelines (AQG) for the PNHs by WHO and the Netherlands

Country	Limit value	Guide value	Measuring Period
Netherlands	5ng/m^{3}	0.5 ng/m^{3}	Year as ng BAP/m^{3}
WHO-AOG	-		Year as ng BAP/m^{3}

Table 7: Proposed Ambient Limits for PNH in India

S .No.	Air Toxic Pollutents	Ambient Air Quality Standard	Ambient Air Quality Standard up
1	Benzene	10 ng/m^{3}	5 ng/m^{3}
2	Benzo(a) Pyrene	5 ng/m^{3}	1 ng/m^{3}

and as an insecticide and fungicide (HSDB 1994; Windholz 1983). Fluorene is used as a chemical intermediate in many chemical processes, in the formation of polyradicals for resins, and in the manufacture of dyestuffs. Phenanthrene is used in the manufacture of dyestuffs and explosives and in biological research (Holloway 1987; HSDB 1994). Fluoranthene is used as a lining material to protect the interior of steel and ductile-iron drinking water pipes and storage tanks (NRC 1983).

Photolysis and Half Life of PNHS in the Environment

Submicron aerosol has a half life of about 5-30 days in the atmosphere thus PNH may be transported and deposited at other surface in very remote region at highly reduced concentration as a result of the effects of atmospheric dispersion and chemical reaction. PNH laden aerosol is transported from air to soil and water via physical processes involving impaction surfaces, gravitational setting and scavenging by rain and snow. Transfer rates are also highly sensitive to particle size. The physical removal or transport of airborne particles is a function of the particles size and meteorological conditions. The occurrence of some PNH in remote areas such as Arctic and marine atmospheres (Mc Veety et. al. 1998) was mainly by aerial transport from distant anthropogenic sources. Half lives of PNH under simulated atmosphere conditions (expressed in hours) are given in Table 2. A number of research workers have demonstrated that may PNH are susceptible to photo chemical and or chemical transformation of PNH by gas-particle interactions in emission plumes, exhaust systems or even during atmospheric transport according to Atkinson, (1987).

Fate of PNHs in the Environment

- PNHs enter the air mostly as releases from burning coal, coke oven plant, automobile exhaust and wood fire.
- PNHs remains in air attached to dust particles.
- Most PNHs do not dissolve easily in water. They stick to solid particles and settle to the bottom of lakes, rivers or soil.
- Microorganisms break down PNHs in soil or water after a period of weeks to months.
- In soil, PNHs are most likely to stick tightly to particles. Certain PAHs move through soil to contaminate ground water.
- PNHs in remote areas such as arctic & marine atmosphere are result of long range transport.

Mode of Exposure and Daily Intake of PNHs

Human exposure to PNH can occur through several environmental pathways due to their numerous sources. However, the occurrence of PNH in urban air has caused particular concern because of the continuous nature of the exposure and the size of the population at risk. The urban atmosphere is a very complex and dynamic system containing a large variety of interacting chemical species in both the gas and particulate phases. PNHs compounds can reach to the human body by four different mode of exposure:

Tobacco/Cigarette Smoking

Tobacco alone accounts for 30% of total morality due to cancer every year. More than 70 PNH compounds have been analyzed in cigarette smoke. Smokers have eight times more probability of cancer attack than non-smoker. In developing countries approximately 30% smokers are young in the age group to 10 – 29 year. About 30-40% of them fall victim of premature death than expected life. The average total BaP content in the main stream smoke of 1 cigarette was 35 ng before 1960 and 18 ng in 1978-1979. Modern low tar cigarettes deliver 10 ng BaP. The concentration of BaP in a room extremely polluted with cigarette smoke was found to be 22 ng/m^3 (WHO 1987). Drinking Water – Examination of number of drinking water has been performed. The concentration of BaP ranges from 0.1 to 23.4 µg L-1, while for other PNHs the concentrations were between 0.001 to 0.01 µg L-1.

Food

American source indicate an intake of total PAHs from food in order of 1.6 – 16 g per day. The contents of BaP in various processed food was repeatedly found to measure up to 50 µg kg-1. The potential doses of carcinogenic PNHs by inhalation range between about 0.02 µg day-1 and 3 µg day-1 with median value of 0.16 µg day-1. This is nearly 20 times less than calculated food dose and about 25 times more than the potential dose with drinkable water. The intake of potential carcinogenic PNHs by non smokers and smokers is given in Table 3. Research up to now has shown that air contributes 3 – 20 % of total human exposure to PAH and comes in second after food.

Human Health Effects of PNHS

As discussed above, PNHs are hydrophobic compounds and their persistence in the environment is mainly due to lower water solubility and electro-chemical stability (CPCB, 2003). Evidence suggest that the lipophilicity, environmental persistence and genotoxicity of PHNs increase as the molecular size of the PNHs increases up to four or five fused benzene rings. More than 200 compounds are tested as possible carcinogens. Among these 25% have been found tumerogenic and about 30% of these were PNH. Lamb et al (1980) reported that BaP is a definite carcinogen with an LD50 of 24 micrograms. In causing health effect, these compounds are primarily activated through an oxidative metabolic pathway to form electrophilic intermediates. Such intermediates can develop covalent bonding with cellular DNA to form DNA adducts. This adducts, if not repaired, may initiate gene mutation and lead to adverse health effect ultimately manifesting in cancer, birth defects and genetic changes. PNHs being highly lipid soluble are absorbed by the lungs and gut of the mammals.PNH also penetrates in to the bronchial epithelium cells where metabolism takes places. International Agency for Research on Caner has classified PNHs according to carcinogenicit (IARC, 1987) as shown in Table 4.

Mechanism of PNH Carcinogenesis

Research has established that the PNH molecules themselves are not carcinogenic agents; rather they must be transformed by several metabolism reactions in the body before the actual cancer causing species is produced (Colin Baird, 1999). The first chemical transformation that occurs in the body is the formation of an epoxide ring across one C=C bond in the PNH. The specific epoxide of interest to the carcinogenic Behavior of B(a)P is shown in Figure 7. A fraction of these epoxide molecules subsequently add H2O, to yield two- OH groups on adjacent carbons as shown in Figure 8. The double bond (shown in the structure above) that remains in the same ring as the two-OH groups subsequently undergo epoxidation, thereby yielding the molecule that is the active carcinogen (Figure 9). By adding H+, this molecule can form a particularly stable cation that can bind to molecules such as DNA, thereby inducing mutations and cancer. The metabolic reactions of epoxide formation and H_2O addition are part of the bodies attempt to introduce-OH groups into hydrophobic molecules like PNHs and thereby make them more capable of becoming water soluble and eliminated. For B(a)P and other PNHs that possess a bay region, one of the intermediate products in this multi step process can be diverted instead into the formation of a very stable cation that induce cancer. The PNHs that are the most potent carcinogens each possess a bay region formed by the branching in the benzene ring sequence, the organization of carbon atoms at a bay region (As shown in Figure 10) imparts a high degree of biochemical reactivity to the PNH. The portion of the total carcinogenic effect of BaP in various particulate emissions is shown in Table 5.

Environmental Monitoring of PAHS and Ambient Limits

USEPA, [1997] has classified PNHs with B(a)P indicator species as a B-2 pollutant that means a probable human carcinogen with sufficient evidence from animal studies and inadequate evidence from human studies. In most of the OECD countries theToxic air pollutants (TAPs) monitoring (Particularly the PNHs, BAP as an indicator species) and the risk assessment has become a regular feature (CPCB, 2003). Integrated and long term monitoring is being carried out in the Netherlands, Sweden and the United States. The world health organization (WHO) has already added PNHs in to the list of the priority pollutants in both air and water. France, Japan, Germany, Netherlands, Sweden and Switzerland have prescribed emission standards for most of TAPs including PNH. The WHO and the Netherlands (WHO, 1987) have even prescribed ambient air quality guidelines (AQG) for the PNHs (Table 6). This will help in the development of data banks of PNH levels in air, formulation and development of standards for ambient air quality, source emissions and effluents, granting consent based on PNHs to the relevant of abatement and control strategies of PNHs in the environment.

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