

**DISTRIBUTION OF POLYCYCLIC AROMATIC  
HYDROCARBONS IN SURFACE SEDIMENTS  
OF RIVER YAMUNA**

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Degree of

**Master of Philosophy**

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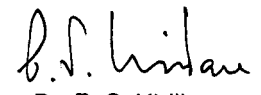
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**CERTIFICATE**

This is to certify that the research work embodied in this dissertation entitled "***Distribution of Polycyclic Aromatic Hydrocarbons in surface sediments of river Yamuna***" has been carried out in this School for the partial fulfillment of the award of the degree of Master of Philosophy. This work is original and has not been submitted in part or full for any other Degree or Diploma in any other University.

  
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*To my dear parents.....*

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## LIST OF ABBREVIATION

*Acen* = Acenaphthene

*Acn* = Acetonitrile

*Acy* = Acenaphthylene

*Anth* = Anthracene

*B[a]A* = Benz(a)Anthracene

*B[a]P* = Benz(a)Pyrene

*B[b]F* = Benz(b)Fluoranthene

*B[ghi]P* = Benz(ghi)Perylene

*B[k]F* = Benz(k)Fluoranthene

*Chry* = Chrysene

*Db[ah]A* = Dibenz(a,h)Anthracene

*Fl* = Fluoranthene

*Flu* = Fluorene

*IP* = Indeno(1,2,3-cd)Pyrene

*Naph* = Naphthalene

*Phen* = Phenanthrene

*Pyr* = Pyrene



## **List of Annexure**

- Annexure I    Structure of PAHs
- Annexure II    Chromatogram of PAHs standard spiked with an internal standard

*Chapter I*

*Introduction*

## INTRODUCTION

The rapid pace of industrialization and the greater emphasis on agricultural growth for overall development have brought in a host of environmental problems in recent years in India. Financial and technological constraints have led to inefficient conversion processes, thereby leading to generation of larger quantities of waste and resulting pollution. The concentration of industries in certain pockets and the skewed distribution of rainfall have further compounded the scenario.

Pollution problems in India are addressed by a combination of legislative, punitive, and motivational measures. The government of India has enacted a number of pieces of legislation, such as the Water (Prevention and Control of Pollution) Act, 1974 and amended in 1988; the Water (Prevention and Control of Pollution) Cess Act, 1977 and amended in 1991; and the Environment Protection Act, 1986, etc.).

All of India's fourteen major river systems are heavily polluted, mostly from the 50 million cubic meters of untreated sewage discharged into them each year (APCSS 1999). In 1995, the Central Pollution Control Board identified severely polluted stretches on 18 major rivers in India (World Bank 1999). Not surprisingly, the majority of the stretches were found in and around large urban areas. According to Central and State Pollution Control Boards there are 1,532 "grossly polluting" industries in India, although almost all industries do not comply with emission standards (World Bank, 1999).

Wastewater from industrial activities is often contaminated with highly toxic organic and inorganic substances, some of which are persistent pollutants and remain in the environment for many years. For instance, over 50% of the urban organic load in some cities originates from industrial effluent, and heavy metal contamination from thermal power, tannery and mining activities has occurred in several locations (World Bank 1999) (<http://www.iupac.org/publications/ci/1999/march/india.html>).

The impact of persistent organic pollutants (POPs) in the environment deserves increasing attention so in recent years scientists have become increasingly concerned about the distribution and fate of POPs, particularly in the tropical and subtropical regions of Asia (Tanabe, 1991; Iwata et al., 1994; Zakaria et al., 2002; Zhang et al., 2002), because the tropical mild to high temperatures and heavy rainfalls are able to rapidly dissipate POPs into the atmosphere and aquatic systems from points of usage or discharge. These compounds are characterized as environmentally stable, bio-accumulable, and toxic which are related to properties such as high chemical stability, hydrophobic, and metabolic disruption potential. These features result in a high capacity of distribution throughout the planet being identified in the most remote areas such as the Arctic and Antarctica (Abarnou et al., 1987).

One of the important group of POPs is polycyclic aromatic hydrocarbons (PAH) and several members of this group - *B[a]A*, *B[b]F*, *B[k]F*, *B[a]P*, *Chry*, *Db[a,h]A*, and *IP* - have been described as mutagenic, carcinogenic, and teratogenic (Bouloubassi and Salot, 1991) being included in the U.S. EPA and the EU priority pollutants lists. They include highly mutagenic and carcinogenic four- to seven-ring compounds (Medical Research Council, 1968). Two- or three-ring PAHs are less mutagenic (Berichte 1/79 des Umweltbundesamtes, 1979) but can be highly toxic, e.g. three-ring phenanthrene and its methyl-substituted homologues are toxic to algal growth (Pulich *et al.*, 1974).

PAHs are multi-aromatic ring systems sometimes called Polynuclear aromatics (PNA) are composed of carbon and hydrogen atoms arranged in the form of fused aromatic rings (linear, cluster or angular arrangement) (Sims and Overcash, 1983). The PAH family includes 660 substances indexed by the National Institute of Standards and Technology (Sander and Wise 1997). Approximately 30 to 50 of them commonly occur in the environment (Grimmer 1983,) but in practice PAHs analysis is restricted to the determination of 6 to 16 compounds. Individual PAHs differ substantially in their physical and chemical properties (Maliszewska-Kordybach, 1999; Sims and Overcash, 1983). The best-known model compound from this group is highly carcinogenic Benzo(a)pyrene (BaP). US Environmental Protection Agency (EPA) has fixed 16 PAHs as priority pollutants, the latest being effective from 1997 (US EPA, 1997 . Mastral *et al.*, 2000). These compounds are as follows: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Chrysene, Benzo(a)anthracene, Benzo(b) fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-c,d)pyrene, Benzo(g,h,i)perylene and Dibenzo(a,h)anthracene. PAH generally occur as complex mixtures and not as single compounds in urban area environmental samples. They appear to be ubiquitous in the biosphere and therefore, a better understanding of their formation, behavior and fate in the environment is necessary.

### 1.1 Physical and Chemical properties of PAHs

PAHs are composed of carbon and hydrogen atoms arranged in the form of fused aromatic rings and their physical and chemical properties are a given in Table 1.1 and Appendix I. They vary quite regularly with the number of rings and the molecular mass. The general characteristics common to the class are high melting and boiling points, low vapor pressures and solubility in water. PAHs are soluble in many organic solvents (IARC, 1983).

Vapor pressure generally tends to decrease with the increase in molecular weight, varying more than ten order of magnitude from low to high molecular weight compounds. This affects the different percentages of individual PAHs, which are adsorbed on particulate matter in the atmosphere, and they are retained with the particulate matter during sampling on filters (Thrane and Mikalsen, 1981). Vapor pressure increases markedly with increase in ambient temperature (Murray *et al.*, 1974), which then additionally affects the distribution coefficients

Table 1.1. Physical and chemical properties of PAHs.

Compounds	Mol. Wt	Abbr.	Mol. Formula	Melting point (°C)	Boiling Point (°C)	Vap. Press. Pa at (25°C)	n-Octanol/Water Partit Log K <sub>ow</sub>	Water solubility (25°C) (µg/L)	Henry's constant (25°C) KPa m <sup>3</sup> /mol
Naphthalene	128	Nap	C <sub>10</sub> H <sub>8</sub>	81	217.9	1.4	3.4	3.17 x 10 <sup>4</sup>	4.89 x 10 <sup>-2</sup>
Acenaphthylene	152	AcI	C <sub>10</sub> H <sub>8</sub>	92-93	265-275	8.8x10 <sup>-1</sup>	4.07	-	1.14 x 10 <sup>-3</sup>
Acenaphthene	154	Acn	C <sub>12</sub> H <sub>10</sub>	85	279	2.9 x 10 <sup>-1</sup>	3.92	3.93 x 10 <sup>3</sup>	1.48 x 10 <sup>-2</sup>
Fluorene	166	Fl	C <sub>13</sub> H <sub>10</sub>	115-116	293-295	8.0 x 10 <sup>-2</sup>	4.18	1.98 x 10 <sup>3</sup>	1.01 x 10 <sup>-2</sup>
Anthracene	178	Anth	C <sub>14</sub> H <sub>10</sub>	216.4	342	8.0 x 10 <sup>-4</sup>	4.5	73	7.3 x 10 <sup>-2</sup>
Phenanthrene	178	Phen	C <sub>14</sub> H <sub>10</sub>	100.5	340	1.6 x 10 <sup>-2</sup>	4.6	1.29 x 10 <sup>3</sup>	3.98 x 10 <sup>-3</sup>
Fluoranthene	202	Flan	C <sub>16</sub> H <sub>10</sub>	108.8	375	1.2 x 10 <sup>-3</sup>	5.22	260	6.5 x 10 <sup>-4</sup>
Pyrene	202	Pyr	C <sub>16</sub> H <sub>10</sub>	150.4	393	6.0 x 10 <sup>-4</sup>	5.18	135	1.1 x 10 <sup>-3</sup>
Benzo(a)Anthracene	228	BaA	C <sub>18</sub> H <sub>12</sub>	160.7	400	2.8 x 10 <sup>-5</sup>	5.16	14	-
Chrysene	228	Chr	C <sub>18</sub> H <sub>12</sub>	253.8	448	8.4 x 10 <sup>-5</sup>	5.91	2	-
Benzo(b)Fluoranthene	252	BbF	C <sub>20</sub> H <sub>12</sub>	168.3	481	6.7 x 10 <sup>-5</sup>	6.12	1.2	5.1 x 10 <sup>-5</sup>
Benzo(k)Fluoranthene	252	BkF	C <sub>20</sub> H <sub>12</sub>	215.7	480	1.3 x 10 <sup>-8</sup>	6.84	2.5	4.4 x 10 <sup>-5</sup>
Benzo(a)Pyrene	252	BaP	C <sub>20</sub> H <sub>12</sub>	178.1	496	7.3 x 10 <sup>-7</sup>	6.5	3.8	3.4 x 10 <sup>-5</sup>
Benzo(ghi)Perylene	276	BghiP	C <sub>22</sub> H <sub>12</sub>	278.3	545	1.4 x 10 <sup>-8</sup>	7.1	0.26	2.7 x 10 <sup>-5</sup>
Indeno(1,2,3-cd)Pyrene	276	IP	C <sub>22</sub> H <sub>12</sub>	163.6	536	1.3 x 10 <sup>-8</sup>	6.58	62	2.9 x 10 <sup>-5</sup>
Dibenzo(a,h)Anthracene	278	DBahA	C <sub>22</sub> H <sub>12</sub>	266.6	524	1.3 x 10 <sup>-8</sup>	6.5	0.5 (27°C)	7 x 10 <sup>-6</sup>

Source : Menichini (1994)

between gas and particle phase (Lane, 1989).

PAHs are non-polar organic hydrocarbons. PAH aqueous solubilities span several orders of magnitude and decrease with increasing molecular weight and the hydrophobicity of the compounds. Aqueous solubilities can be described using the octanol-water partitioning coefficient ( $K_{ow}$ ). Low molecular weight; volatile PAHs with less than four rings are water-soluble with a low affinity for particle adsorption ( $\log K_{ow} < 5$ ). PAHs with high molecular weights are generally water insoluble and have a strong affinity for adsorption onto particle surfaces that are suspended in air and water ( $\log K_{ow} > 5$ ). PAH properties such as sorption/desorption, partitioning, and availability to biota etc, are directly or indirectly related to their solubilities or hydrophobicity. Compound with very low water solubility or very high hydrophobicity tends to leave the truly dissolved state and bind to solid materials and becomes less available to the receptors. Since PAHs possess lipophilic properties, they tend to associate with organic matter containing fatty acids and waxes such as plant membranes and cuticles.

PAHs are chemically inert compounds. When PAHs react, they undergo two types of reactions, i.e. electrophilic substitution and addition reactions. The former is preferred since it does not destroy the aromatic character of PAHs, while addition is often followed by elimination resulting in a net substitution. Following photodecomposition, in the presence of air and sunlight, a number of oxidative products have been identified particularly quinones and endoperoxides. Various experimental studies have revealed reactions of PAHs with nitrogen oxides and nitric acid to form nitro derivatives as well; with sulfur dioxide and sulfuric acid in solution to form sulfinic and sulfonic acids. PAHs may also be attacked by ozone and hydroxyl radicals, which are present in the atmosphere. The formation of nitro-PAH is particularly important owing to their biological impact, and to their mutagenic activity (Howard et al., 1990)

In general the mentioned reactions are of interest with regard to the environmental fate of PAHs, but the results of experimental studies are difficult to interpret because of complexity of interaction occurring in environmental mixtures and difficulty in eliminating artifacts during analytical determinations. These reactions are also considered for possible PAHs losses during the ambient atmospheric sampling (Menichini et al., 1992a)

## 1.2 Formation of PAHs

PAHs are formed in all processes of incomplete combustion of organic substances (Lenicek et al., 1997; Sims and Overcash 1983; Wild and Jones 1995). Their production is favored by an oxygen deficient flame, temperatures in the range of 650-900°C and fuels, which are not highly oxidized.

According to the formation mechanisms, PAHs can be classified as pyrolytic and petrogenic PAHs. Pyrolytic PAHs are formed as a consequence of incomplete combustion whereas petrogenic PAHs are mainly derived from crude oil and its refined products. Pyrolytic and petrogenic sources are known to generate substantially different PAH assemblages. High

temperature combustion processes such as the incomplete combustion of fossil fuel, generate PAH mixtures, which are quantitatively similar, regardless of the fuel material burned (LaFlamme and Hites, 1978; Prahl and Carpenter, 1983; and references therein). Here, the predominant PAH compounds are the parent or non-alkylated compounds, and only relatively minor levels of alkylated homologues are present. In contrast, PAH mixtures in unburnt fossil fuels contain higher levels of alkylated PAH than corresponding non-alkylated PAH structures. The relative abundance of PAH compounds is dependent on the source temperature and low-to-moderate source temperatures may result in PAH assemblages with intermediate characteristics to those just described (LaFlamme and Hites, 1978). In general, combustion PAH assemblages are dominated by relatively high molecular weight compounds with three condensed rings or more, whereas, mono-, bi- and tri-cyclic aromatic compounds are most abundant in fossil fuel PAH mixtures (Prahl and Carpenter, 1983).

### 1.3 Sources of PAHs

Airborne particulates carrying PAHs, are transported worldwide in the atmosphere, and usually find their final destination in soils, and in sediments of aquatic systems [Christensen et al., 1997].

The major sources of formation of PAHs can be of two category viz. anthropogenic and natural. Anthropogenic sources can be divided into two categories viz. the combustion of materials for energy supply (e.g. coal, oil, gas, wood, etc.) and combustion for waste minimization (e.g. waste incineration) (Ramdahl et al., 1982; Wild and Jones, 1995). The first category includes stationary sources like industries (mainly coke and carbon production, petroleum processing, aluminum sintering, etc.), residential heating (furnaces, fireplaces and stoves, gas and oil burners), power and heat generation (coal, oil, wood and peat power plants) and mobile sources like cars, lorries, trains, aeroplanes and sea traffic (gasoline and diesel engines). The second category covers incineration of municipal and industrial wastes. Other miscellaneous sources are unregulated fires such as agricultural refuse burning, recreational fires, crematoria etc., cigarette smoking as well as volatilization from soils, vegetation and other surfaces (Ramdahl et al., 1982; Wild and Jones, 1995).

Volcanic eruptions and forest and prairie fires are among the major natural sources of PAHs to the atmosphere but do not significantly contribute for the present overall PAHs emission. Direct PAH biosynthesis by organisms such as bacteria, fungus, and algae has not yet been clarified (Parlanti, 1990). Perylene is a good example of a PAH substance of biological origin found in both marine and freshwater sediments (Wakeham et al., 1980; LaFlamme and Hites, 1978). The derivatives from biogenic precursors like terpenes, pigments and steroids are also the important PAHs composition in marine environment (Wakeham et al., 1980; Sporstol et al., 1983; Budzinski et al., 1997).

Indeed, PAHs can be produced diagenetically during the evolution of organic matter in

sediments (Benlahcen et al., 1997) and from the short-term degradation of biogenic precursors (Baumard et al., 1998). The deposition of suspended particles carried by rivers will also augment the local accumulation of PAHs (Guzzella and Depaolis, 1994).

Polycyclic aromatic hydrocarbons (PAHs) are widespread pollutants in aquatic systems. PAHs can be introduced into the coastal environment by various processes. PAHs of coastal sediments are due to both anthropogenic and natural sources (NRC, 1983, 1985). However, several studies have indicated that the anthropogenic input of PAHs to aquatic sediments far exceeds natural sources [National Academy of Sciences (NAS)].

Among anthropogenic factors, petrogenic and pyrolytic sources are the most important. Although somewhat controversial, the aromatisation of cyclic compounds could be a further source of PAHs (LaFlamme and Hites, 1978). Whereas pyrolytic sources include combustion processes (e.g., fossil fuel combustion, forest fires, shrub and grass fires), the petrogenic input is closely related to petroleum products (e.g., oil spills, road construction materials). The former inputs (anthropogenic combustions) are largely prevalent in aquatic environments. Major human activities which produce PAHs include pyrolysis of wood to produce charcoal and carbon black, coke production, manufacturing of gas fuel, power generation from fossil fuels, combustion of fuels in internal combustion engines, incineration of industrial and domestic wastes, oil refinery and chemical engineering operations, aluminum manufacturing, etc. By-products of these processes, which contain significant amount of PAHs, have been dumped on the land, in the water, or buried at subsurface sites.

PAHs also find their way directly into the aquatic environment through discharges from various human activities, including: industrial and domestic sewage effluents, spills and leaks of PAH-containing materials such as oils; runoff from paved roads, parking lots, the grounds of wood preservation plants; offshore drilling; and leaching and disposal of refinery effluents. (Ogunfowokan et al., 2003; Sanders et al., 2002)

Industrial wastes and domestic sewage also contains high concentrations of particulate and soluble PAH, and together with surface runoff from land and fallout from air, represent the main sources of high molecular weight PAHs into the aquatic environment. PAHs account for approximately 20% of total hydrocarbons present in crude oil, and are the most metabolically toxic of all the petroleum compounds (Neff, 1990). Oil spillage is a global problem where for example, in 1999 approximately 32.2 million gallons (109,400 tons) of oil were spilled worldwide into marine and terrestrial environments as the result of over 250 incidents. (Peters *et al.*, 1995; Lockhart *et al.*, 1992).

#### **1.4 Fate of PAHs**

Their widespread occurrence is essentially due to formation and release during the incomplete combustion of organic matter (Wakeham et al., 1980). Depending on their physicochemical properties, atmospheric PAHs are distributed between the gas and particulate



phases, mainly in association with small particles ( $<1 \mu\text{m}$ ) (Aceves and Grimalt, 1993; Baker, 1990; Leister and Baker, 1994; Allen et al., 1996). PAH in the atmosphere can enter the water column by gas exchange across the air-water interface, dry deposition of airborne particulate matter, or wet deposition by rainfall (McVeety and Hites, 1988; Simcik et al., 1996; Gustafson and Dickhut, 1997; Dickhut et al., 2000; Tsai et al., 2002). The volatile PAH (two to three rings), which occur in relatively high amounts as alkylated congeners, are derived mainly from combustion emissions of vehicles that use petroleum-derived fuels and lubricants (Marcus et al., 1988; Rogge et al., 1993; Schauer et al., 1999, 2002). The four to six ring non-volatile or soot PAH derived from high-temperature combustion processes and are transported into the water column primarily by atmospheric deposition of soot particles. It has been suggested that soot formed from combustion processes plays a major role in PAH cycling in the estuary (Maruya et al., 1996; Pereira et al., 1999). Because PAH are minor components in petroleum, boats and other watercraft can introduce refined petroleum and combustion-derived PAH to the water column through their engine emissions (Wachs et al., 1992; Mastran et al., 1994). Additionally, PAH can enter the water column through urban runoff (Hoffman et al., 1984, 1985). Once in the water column, these dissolved PAH bind to suspended particulate matter due to their hydrophobic properties and can be transported to the surface sediments. PAH are generally major components of the total extractable organic matter present in sediments and are minor components in water. Sediments are therefore good environmental compartments for the record of the long-range distribution patterns of these compounds. In this respect, reported data have shown relatively high levels of sedimentary PAH in rural and remote regions, in some cases not being significantly different from those reported in locations close to centers of human activity (Baker, 1990; Simcik et al., 1996).

Chronic introduction of PAHs in estuaries can affect freshwater quality and induce accumulation in the pelagic and benthic food chains at various trophic levels leading to long-term changes in the biota. The food chain, the principle pathway to humans, is through the consumption of fish, shellfish and crustaceans (Varanasi et al., 1989). Some PAHs are readily degradable. Their occurrence on airborne particles, riverine suspensions or sediments suggests that part of them survive degradation processes. It has been hypothesized that PAHs adsorbed onto particles are more readily accessible to degradation whereas those tightly bound or occluded into particles may survive atmospheric or water transport (Readman et al., 1984). Because of differences in particle association, combustion-derived PAHs have a longer residence time in the environment than oil-derived ones (Readman et al., 1982; Jones et al., 1986). Furthermore, low molecular weight PAHs, which dominate fossil fuel assemblages, are more labile. Approximately 80% of the low molecular weight phenanthrene and anthracene input can be lost from the water surface to the atmosphere through volatilization (McVeety and Hites, 1988).

### 1.5 Sediment as sink for PAH

High concentrations of PAHs in sediments are usually high in highly industrialized and urbanized locations such as North America [Ashley and Baker, 1999], Canada [Simpson et al., 1996], and Germany [Witt, 1995]. The detected total PAH concentrations in sediments can be higher than 10,000 mg/g dry weight [Simpson et al., 1996]. It is well known that they are sensitive indicators between natural and anthropogenic variables (Salomons, 1995; Calmano et al., 1996).

Sediments are deposited material consisting of organic matter in various stages of decomposition, particulate mineral matter and inorganic material of biogenic origin (Viguri et al., 2002; Luca et al., 2004). A key distinction between the soil and sediment systems is particle size composition and its potential impact upon environmental behavior. Sediments are largely eroded soils that have been subjected to continuous re-dispersion and particle-size fractionation commencing with runoff and continuing with subsequent water-system processes. These processes are highly dependent upon the dynamics of the specific stream, river, pond, or lake and upon the dispersion properties of the parent soil. One result is that sediment within a given water compartment may contain a very narrow range of particle sizes. For example, suspended sediment within a river system may be largely clay, bottom sediment from the middle of the river largely sand, and bottom sediment from the edge largely silt. Functional dependence on particle size could vary the degree of sorption in different river compartments or produce a nonuniform distribution of sorbed pollutant within the sediment (Karickhoff et al., 1979).

Once formed PAHs enter the near shore and water directly from the air with dust and precipitation or on particles washed from the soil by runoff (Environmental Canada (2001). PAHs dissolved in water can be 'taken up' by plants and are released to soil and water when the plant dies, decompose or are burned. PAHs also find their way directly into the aquatic environment through discharges from various human activities, including: industrial and domestic sewage effluents, spills and leaks of PAH-containing materials such as oils; runoff from paved roads, parking lots, the grounds of wood preservation plants; offshore drilling; and leaching and disposal of refinery effluents. (Ogunfowokan et al., 2003; Sanders et al., 2002)

Once PAHs are introduced into the environment and due to their hydrophobic character and high partition coefficients, they are strongly sorbed onto the surface of suspended particles associated with the organic compounds of solid phase matrix particles and hence sediments (Readman et al., 1984; Ko and Baker, 1995.). In the long term, estuarine sediment that contains large pools of organic matter can be a significant repository for PAHs (Pereira et al., 1999). Sediment retention capacity for PAHs can be related to their physio-chemical properties such as organic carbon content, grain-size, and reaction of diagenesis etc. Previous results have demonstrated that the sorption of hydrocarbons is related to the organic matter of the sediments (Yunker et al., 1996; Baumard et al., 1998, Karickhoff et al., 1979; Karickhoff., 1981; Boehm and Farrington, 1984). Besides these parameters, origin of PAHs affects their accumulation

and distribution in the sediments (Hostettler et al., 1999).

Once deposited in sediments, these compounds are less subject to photochemical and biological oxidation and thus tend to persist for longer periods and to accumulate in high concentrations (Liu et al., 2000). PAHs ubiquity in the sediments indicates that accumulation phenomena dominate degradation processes in sedimentary matrices (Soclo et al., 2000). Sediments in particular are 'sinks' where chemicals tend to concentrate.

Sediment bioassays that measure the toxic effects of contaminated sediments on the test organisms have been recently developed and a large variety of bioassays is becoming available. They provide information on the toxicity of contaminated sediments that can be neither derived from chemical analysis nor from ecological surveys (Chapman and Long, 1983; Long and Chapman, 1985). Testing procedures have included numerous techniques such as static tests, flow-through tests and elutriate tests (Burton and Scott, 1992; Schuytema et al., 1996; Mac et al., 1990; Malueg et al., 1984).

Although PAHs appear to be delivered uniformly to remote sites, sediment sites near urban and industrial areas have much higher PAHs concentrations and concentrations are usually found to increase near industrialized areas and continue to increase as urbanization increases (ATSDR 1999a; Gig *et al.*, 2001; Environment Canada, 2001) due to the specific anthropogenic inputs of PAHs such as industrial wastewater and street-dust runoff discharges, deposition of fossil fuel combustion particles and carbonized coal products spills (Hites et al., 1977; Gschwend and Hites, 1981; Witt and Trost, 1999).

### **1.6 Fate in sedimentary matrix**

Although the sources and distribution of PAHs in soils and sediments have been studied fairly extensively, the transport and fate of PAHs on soil sediment surfaces are poorly understood. In addition, the physical and chemical properties, which govern the interaction of the PAHs and substrates, have not been characterized or quantitated.

Due to the nature of hydrophobicity, PAHs tend to reside or partition into the matrices of the non-aqueous phases such as soil and sediment or an oily phase if present. Upon entering an aquatic system, PAHs will rapidly deposit into the sediment or soil and physically adsorb on the solid surface (adsorption) or partition into the organic fraction of the sediment (absorption), and both processes are termed as sorption (Pignatello et al., 1996). This has led to a legacy of PAHs in the environment that now constitutes a source of contamination through desorption. The desorption process is of even more interest to environmental scientists because it is the corresponding aqueous phase concentration that drives risk assessment, regulation and remediation efforts (Beckles, 2000). The sorption and desorption of organic chemicals to soils and sediments is a complex process, given the diversity, magnitude, and activity of chemical species, phase, and interfaces commonly present in contaminated subsurface environments.

The fate of hydrophobic organic pollutants (compounds having a water solubility of less

than a few parts per million) in a water/sediment or water/soil system is highly dependent upon their sorptive behavior (Stumm and Morgan, 1970). The sorption behavior of PAHs has been widely studied, both in field situations. (Zhou et al., 1998; Readman et al., 1984; Zhou et al., 1996; Zhou et al., 1999) and under controlled conditions, (Turner et al., 1999) and is highly influenced by the environmental conditions under which sorption takes place. As a result, sorption is dependent on a number of parameters including those related to water such as salinity and colloids (Zhou et al., 1996) and those related to suspended particulate matter such as concentration, particle size, particle surface area, particulate organic carbon (POC) content (Zhou et al., 1998; Readman et al., 1984, Zhou et al., 1999). It is expected that the sorption of PAHs by particles is a complex process involving the interplay between PAH compounds, water and sediment.

Sorption to sediment is a key process in determining the actual fate and risk of hydrophobic organic chemicals (HOCs) in aquatic environments. It lowers aqueous concentrations and therefore reduces mobility, bioavailability, and chemical and biological degradation processes. Because of their hydrophobic nature, HOCs predominantly sorb to the hydrophobic regions that are present in sediments (Karickhoff, 1979; Ghosh et al., 2000). The volumetrically most important sedimentary hydrophobic domain is natural organic carbon, the degradation product of dead biomass. Therefore, sorption is commonly described as being a function of the organic carbon content in sediments. It has been assumed that HOCs show simple partitioning between the sediment organic carbon and the surrounding aqueous phase, which can be expressed in terms of an equilibrium-partitioning coefficient ( $K_{oc}$ ). Karickhoff et al. (1979) have described the sorption behavior of a number of hydrophobic molecules including some PAHs on sediments. They suggested that the sorption of such molecules appears to be determined by the organic carbon content of the substrate. They further suggested that the sorption constant  $K_{oc}$ , which is derived from the linear partition coefficient  $K_p$  and the organic content of the sorptive substrate (fractionated sediment fines), could be related to the solubility of the compound and to the solvent partitioning of the compound (e.g., octanol-water partition coefficient,  $K_{ow}$ ). However, numerous studies have revealed that the application of this so-called organic carbon equilibrium partitioning model often leads to an overestimation of aqueous concentrations in field situations (e.g., refs Gustafsson and Gschwend, 1997; Naes et al., 1998; TenHulscher et al., 1997; Jonker and Smedes, 2000) and, therefore, an overestimation of bioaccumulation (Paine et al., 1996) and toxic effect to aquatic organisms (Paine et al., 1996; Naes et al., 1999). In other words, HOCs often show much stronger sorption to sediments than can be expected on the basis of hydrophobic interactions only. A general hypothesis that was brought up to explain this phenomenon is that contaminants slowly diffuse into mineral micropores or nanovoids located in "hard glassy" or "condensed" organic matter (Pignatello and Xing, 1996; Pignatello, 1998). Here, the chemicals are being "sequestered", which makes them more resistant to the desorption process (Luthy et al., 1997). However, since a lot of resistant

sorption data concern polycyclic aromatic hydrocarbons (PAHs) (Gustafsson and Gschwend, 1997), also another more specific hypothesis was introduced. PAHs are mostly formed during incomplete combustion processes together with a condensed particulate carbon phase, which is commonly referred to as "soot". Pyrogenic PAHs are suggested to be partially occluded in the soot matrix during this co-production process (McGroddy and Farrington, 1995; Readman et al., 1984), to be trapped in micropores, or to have extremely high affinities for the aromatic flat surfaces of soot (Gustafsson and Gschwend, 1997). This would also result in reduced partitioning of sedimentary PAHs to the aqueous phase if the chemicals have a pyrogenic origin. Indeed, it was recently demonstrated that sorption of both added (Bucheli and Gustafsson, 2000) and natively bound PAHs (Jonker and Koelmans, 2001) to soot is exceptionally strong as compared to regular hydrophobic partitioning into natural organic carbon. Another recent study has shown that not only PAHs but also other organic chemicals may possibly exhibit enhanced sorption to soot (Jonker and Smedes, 2000). Because of its presumed high sorption and sequestration capacity, in some cases soot may also be responsible for very slowly desorbing fractions of (planar) HOCs in sediments (e.g., in Lake Ketelmeer; TenHulscher et al., 1999). Similar fractions were recently observed for PAHs in coal (Ghosh et al., 2000; Karapanagioti et al., 2000), a material that from a physicochemical point of view may be defined as "soot-like".

In addition to affecting the physical movement of pollutants, sorption can be involved directly in pollutant degradation via surface-associated chemical processes. Moreover, natural sediments can indirectly mediate solution-phase processes by altering the pollutant concentration in solution or by providing a buffered solution-phase ion suite that may affect the dielectric properties and acidity of the solution phase. A realistic key to predicting the environmental fate of hydrophobic compounds then, lies in an understanding of sediment-related processes (Karickhoff et al., 1979).

It is believed that the environmental fate and behavior of hydrophobic organic compounds is ultimately determined by the physicochemical properties of each compound and sediment (Baker et al., 1991; McKenzie-Smith et al., 1994; Doong et al., 2002). A positive linear relationship has been demonstrated between PAH concentrations and the total organic carbon (TOC) in sediment (Witt, 1995; Simpson et al., 1996). However, a poor relationship between sediment grain size and total PAHs in sediment from Baltimore Harbor was also reported (Jeffery and Baker, 1999). Simpson et al. (1996) depicted that the relationship between total PAHs and organic carbon of sediment was only significant for highly contaminated sites where total PAHs were more than 2000 ng/g. This depicts that factors such as site specificity and proximity to sources may be the important factors for the determination of the dominance of contaminants in sediments.

## 1.7 Eco-toxicological significance of PAHS

The main environmental significance of PAHs arises from the fact that some of the PAHs have been identified as carcinogens (to both humans and other animals) and some are classified as mutagenic e.g. *Db[a,h]A*, *B[a]P*, and *B[g,h,i]P* (Hall and Glower, 1990; Marvin *et al.*, 1995).

The retrospective evaluation of the biological significance of chemical residues in sediments is fraught with difficulties if there are no contemporary biological measurements. This is particularly the case for relatively insoluble and adsorptive substances like PAH (NRCC, 1983; Mackay *et al.*, 1992), and is even a problem when evaluating the significance of PAH in seawater due to their tendency to be associated with suspended solids and dissolved organic matter (Law *et al.*, 1997). This has now been recognized by the International Council for the Exploration of the Sea (IC ES, 1996), which recommends that future marine monitoring programmes should fully integrate chemical and biological measurements. The results of the following analysis must therefore be treated with considerable caution.

The fundamental problem involved in assessing the significance of PAHs in sediments concerns their bioavailability. There is no doubt whatever that a variable proportion of sediment-associated PAH is available for uptake by both demersal fish (e.g. Munkittrick *et al.*, 1995; Hellou *et al.*, 1995) and benthic invertebrates (e.g. Landrum *et al.*, 1991; Forbes *et al.*, 1996), and that a major factor determining this proportion is the amount of organic matter present (DeWitt *et al.*, 1992). This in turn controls the percentage, which is strongly adsorbed and therefore less available for uptake via the interstitial water. However, the situation is complicated by the fact that the high MW PAH are more strongly adsorbed than the lighter molecules (Mackay *et al.*, 1992), which means that the former are more strongly bio-accumulated by non-selective deposit feeders than by organisms which merely live in the sediment, but feed on the overlying detritus or plankton (Meador *et al.*, 1995). In other words, the lifestyle of the organism in question will greatly influence its exposure to sedimentary PAH, and direct consumption of particulates can contribute a significant fraction of the total.

Yet another factor influencing exposure is the ability of sediment dwellers to metabolize these compounds. Although some invertebrates (e.g. certain polychaetes, Forbes *et al.*, 1996) are able to degrade and excrete PAH, many are not able to do this well (e.g. bivalve molluscs; Eertman *et al.*, 1995). Furthermore, PAHs are very efficiently metabolized by the Phase 1 enzymes of the cytochrome P450 mixed function oxygenase system in fish liver, and are rapidly excreted as the hydroxylated metabolites in bile (e.g. Hellou *et al.*, 1994; Livingstone *et al.* 1993). Thus, although fish are exposed to sedimentary PAH via several routes (direct contact with sediment; respiration of interstitial water; incidental ingestion of sediment; feeding on contaminated invertebrates), they do not generally accumulate high residue levels. However, this does not mean that they are immune from adverse effects.

Although very high concentrations of sedimentary PAH can be lethal to fish (e.g. Roberts *et al.*, 1989, showed that the 28 day LC50 of a field-collected sediment to spot (*Leiostomus xanthurus*) was in the range 81,000-322,000 µg/kg dry weight LPAH), probably the major concern with respect to the impact of PAH on fish in aquatic sediment systems is the carcinogenicity of some congeners. At least six (B[a]A; Db[a,h]A; B[b]F; B[k]F; Chry and B[a]P) of the PAHs found in the study by Woodhead *et al.* (1999) are known to be carcinogenic in mammals (IARC Working Group, 1983) and are almost certainly so in fish. Others, however, (e.g. *Pry*, *Fl* and *Anth*) do not show carcinogenic activity, although they may be acutely toxic at high concentrations. The cytochrome P450 system, while metabolizing the former PAH to more easily excretable compounds, produces a range of carcinogenic and mutagenic intermediates such as diol epoxides which can lead to the induction of liver carcinomas, at least partly via the formation of PAH-DNA adducts (Van Der Oost *et al.*, 1994; Van Schooten *et al.*, 1995). Concentrations of  $\Sigma$ PAH in sediment as low as 1000 and 3100 µg/kg dry weight, respectively, are able to induce the cytochrome P450 enzymes in winter flounder and spot (Payne *et al.*, 1988; Van Veld *et al.*, 1990), and even lower  $\Sigma$ PAH concentrations (approx. 2-3 µg/kg) have been claimed to cause such effects in fish from the Skagerrak (Forlin *et al.*, 1996), although it seems probable that other substances (e.g. organochlorines) were also contributing to the observed responses (Magnusson *et al.*, 1996). In cases where relatively small levels of cytochrome P450 induction have been measured, one should of course be cautious in concluding that it will inevitably lead to carcinogenesis, even if exposure is prolonged.

There are, however, well-established associations between neoplastic and pre-neoplastic disease in flatfish livers, cytochrome P450 induction, and areas of PAH contaminated sediments (e.g. Malins *et al.*, 1988; Myers *et al.*, 1990; Stein *et al.*, 1990; Collier *et al.*, 1992; Baumann and Harshbarger, 1995; Vethaak and ap Rheinallt, 1992), although the picture in the field is usually complicated by the simultaneous presence of polychlorinated biphenyls (PCB) which also induce the P450 system. The PAH concentrations in sediment which have been associated with liver cancer in fish are variable. For example,  $\Sigma$ PAH concentrations as low as 181 and as high as 41,200 µg/kg dry weight have been associated with carcinogenesis in brown bullhead catfish from Lake Munuscong and the Cuyahoga River, respectively (Baumann *et al.*, 1991), and a few neoplasms were still observable in this species after sediment  $\Sigma$ PAH in the Black / River had dropped to 4270 µg/kg dry weight following remediation measures (Baumann and Harshbarger, 1995). The classic work by Malins *et al.* (1984) in Puget Sound showed a reasonably strong positive correlation coefficient (0.58) between the prevalence of liver disease in English sole (*pteuronectes vetulus*) and the concentration of  $\Sigma$ PAH in sediment. The prevalence of total hepatic lesions was about 20% when the  $\Sigma$ PAH concentration was above approximately 6,000-15,000 µg/kg, although high levels of PCBs and metals were also present. It should be noted that the causal link between PAH exposure and fish liver cancer has not been fully demonstrated under laboratory conditions due to the fact that hepatic carcinomas tend to

develop slowly and generally appear in older fish.

Although neoplastic changes are probably the most sensitive indicator in fish, they are not the only known type. Potentially the most important additional effects are on the immune system, which could result in impaired responses of fish to disease challenges. For example, it has been shown by Payne and Fancey (1989) that American flounder exposed for four months to sediments contaminated with the PAHs found in crude oil ( $\Sigma$ PAH 25,000-50,000  $\mu\text{g}/\text{kg}$ ) develop reduced numbers of melanomacrophage centers in liver, an integral component of the cellular immune system. Furthermore, as little as 1500  $\mu\text{g}/\text{kg}$ ,  $\Sigma$ PAH in sediment can reduce the growth of larval surf smelt (as measured by their DNA content) over a period of 96 h, thus further weakening their resistance to disease and other stressors (Misitano *et al.*, 1994). Some PAH also appear to show endocrine disrupting ability. For example, there is *in vitro* evidence for the anti-oestrogenic action of Acenaphthene, B[a]A, B[a]P, Db[ah]A and several others (Tran *et al.*, 1996; Chaloupka *et al.*, 1990), and some are able to reduce levels of testosterone in male fish and oestradiol in females (Thomas, 1990; Truscott *et al.*, 1983). More recently, Nagler and Cyr (1997) have shown that exposure of maturing male American plaice to  $\Sigma$ PAH in sediment at a concentration of 39,800  $\mu\text{g}/\text{kg}$  dry weight for the five months before spawning affects sperm viability and leads to a 48% reduction in the hatching success of larvae from the eggs of unexposed females.

Much less is known about the modes of toxic action of PAH in invertebrates, although as in fish, relatively high concentrations in sediments can be lethal. For example, Plesha *et al.* (1988) showed that 10,000  $\mu\text{g}/\text{kg}$  of phenanthrene caused significant mortality in the amphipod *Rhepoxynius abronius* during a 10 day exposure, and sediments collected from the field in which PAHs are the principal contaminant have also been shown to exert acute toxicity to invertebrates (e.g. Swartz *et al.*, 1989). Overall, amphipods appear to be of greater acute sensitivity to sediment-associated PAH than fish, and sublethal effects on osmoregulation in grass shrimp have been shown at  $\Sigma$ PAH concentrations in field-collected sediment as low as ~6000  $\mu\text{g}/\text{kg}$  (Alden and Butt, 1987). Furthermore, suspended sediment ( $\Sigma$ PAH = ~32,000  $\mu\text{g}/\text{kg}$ ) from a contaminated harbor has been shown to cause a variety of neoplasms in adult oyster after 30-60 day exposures, although a number of other contaminants were also present (Gardner *et al.*, 1991). It has also been observed that exposure to ultraviolet (UV) radiation increases the toxicity of PAH-contaminated sediments to crustaceans and annelids. For example, Ankley *et al.* (1994) obtained 100% mortality in 10 day sediment tests with the amphipod *Hyatella azteca* and the annelid *Lumbriculus variegatus* in UV-exposed (10% of ambient solar intensity) naturally-contaminated sediments containing about 1000  $\mu\text{g}/\text{kg}$   $\Sigma$ PAH, whereas the same sediment held under fluorescent light produced only 35% and 15% mortality, respectively.



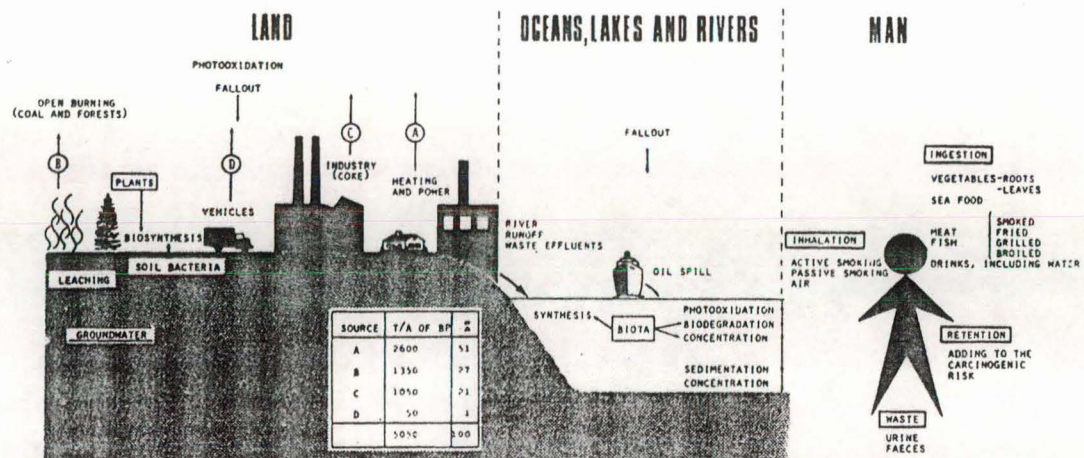
## 1.8 PAHs cycle in Environment

In the air, PAHs can be carried over long distances, stuck to the surfaces of small solid particles and even remote ecosystems have been contaminated. PAHs return to earth in rainfall or particle settling, or alternatively they can break down to longer lasting products by reacting with sunlight and other chemicals in the air over a period of days to weeks (Fig 1.1). As mentioned earlier PAHs are transformed to products, such as nitro-PAH and hydroxy-PAH that are more carcinogenic than the parent compounds. A modeling study opined that reaction with OH radicals was a major route for removal of gas phase fluoranthene and phenanthrene. Wet deposition in the form of snow accounted for majority of PAH removal from the atmosphere in winter. In water, PAHs do not generally dissolve easily, but tend to stick to particulate matter. PAHs stuck to small particles may be found in the surface microlayer, but those stuck to larger particles will settle as sediments. In soil and water, breakdown generally takes weeks to months and the action of microorganisms is usually primarily responsible for this. Some PAHs can build up in living tissue (bioaccumulation) and so the PAH content of plants, invertebrates and fish can be many times higher than the content of the PAH in soil and water. Bio-concentration factors (BCF) (which express the concentration in the tissues compared to the concentration in water) for fish and crustaceans are frequently in the 10-10,000 range, although a BCF of 134,000 has been reported for Benzo[a]pyrene in water flea (*Daphnia pulex*). Bottom dwelling invertebrates and fish can certainly accumulate sediment associated PAHs, but extensive bio-magnification up the food chain is not likely to be a factor because high trophic level consumers, such as humans, can metabolize these substances.

## 1.9 Water pollution in the scenario of River Yamuna

The Yamuna catchments area of the National Capital Territory is one per cent of the river's total catchment area but it generates more than 50% of the pollutants found in the Wastewater with little or no oxygen flows through this stretch. TERI (Terivision, 2002, 46 ) studies points that more than 70% of the 84 districts that make up the Delhi sub-basin, are water-stressed due to depletion and degradation of quality of ground and surface water resources. Delhi receives relatively clean water and converts it into a deadly concoction of disease-bearing water for the people who live downstream.

Eighty per cent of the districts suffer because of that 22-km stretch where effluents pour into the river. Yamuna before the Wazirabad stretch has appreciable levels of dissolved oxygen, low biochemical oxygen demand levels and the water is extensively used for irrigation purposes. Haryana, Himachal Pradesh and parts of Uttar Pradesh use 6000 million metres cubic water every year for irrigation. The scene changes dramatically once the waters reach Delhi. None of the cities downstream generate more than 1000 MLD (million liters per day) of wastewater. In contrast, Delhi alone generates 3000 MLD of wastewater. Bacteriological count – an indicator of the presence of pathogens – is under permissible level upto Delhi. The Delhi



The environmental cycle of PAH.

Fig 1.1. PAHs cycle in Environment

region makes this count dangerously high. This means that Delhi could be responsible for all water-borne diseases caused by use of Yamuna waters beyond Delhi.

In Delhi there are the low-income group and incidentally the high-risk group, which resides on the riverbanks. Though Delhi collectively contributes to the pollution of the river, more than 750 000 colonies along the 22 km stretch bear maximum brunt of the river's waters.

Significantly, even as Delhi generates more than 3000 MLD of wastewater, generally most of its sewage treatment plants function erratically. This simply means that this wastewater enters the Yamuna without undergoing purification.

Large quantities of complex organic pollutants are broken down by aquatic microorganisms who consume dissolved oxygen for this purpose from the waters. This results in depletion of oxygen and hence acute deficiency of oxygen for other riverine organisms such as fish. Plainly speaking, no oxygen means very less life is possible in these waters and the Yamuna becomes a dead river (TERI vision, 2002, 46).

In the current Indian scenario, especially after the economic liberalization in 1991, the motor vehicle population is increasing rapidly, leading to corresponding increase in PAH emissions. (<http://www.ias.ac.in/resonance/Sept2003/pdf/Sept2003p20-27.pdf>).

In spite of very high toxic potency of PAH, in India, environmental monitoring and assessment of PAH is rarely done as compared to European countries and US. In India, apart from this study, very few comprehensive programmes have been taken up for determining the PAHs in sediments. Further, no official norms have been laid for PAHs in air, water and sediment. As Delhi stretch of Yamuna river is highly polluted, this study is planned to provide a preliminary database on the levels of PAHs in sediments of this particular stretch.

## **1.10 Area of study**

### **1.10.1 Delhi and its environment**

Delhi is situated at a latitude of 28°24'17 " to 28°53' and the longitude of 76°20'37" to 77°20'37" with an altitude of 216m above mean sea level. To the north the Himalayas are at distance just 160km and to the south are the central hot plains. To the west of Delhi is the Great Indian Desert (Thar Desert) of Rajasthan and the cooler hilly regions to the north and east.

### **1.10.2 Physiography**

The Union Territory of Delhi consists of flat and level plains interrupted by cluster of sand dunes and a long continuous chain of rocky ridges. The sand dunes are of varying

dimensions and in general trend northeast - southwest. The crests of the dunes generally lie between 6 and 15 metres above the surrounding plains. They are more or less fixed in this area and support vegetation. The plains on the either side of this ridge slopes away from it. Due to its abundant trees and plant life, the ridge is often called as 'lung of Delhi'. Physiographically, 3 segments make the Delhi territory: i) the Yamuna flood –plain ii) the basin area, west of the flood plain, called Dabar iii) the rocky outcrop of Aravalli called Kohi. The shape of the city can be said as circular with radial patterns.

The river Yamuna that enters from the northeastern ridge, passes through Shahdara block and marks the southeast boundary of the territory. It traverses some 40km. in Delhi and has an average bed width varying from two to three km. The treated, partially treated or untreated wastewater generated from the capital city finds its way into the river or canals by twenty-two major drains. Out of these, twenty drains join Yamuna directly while two drains join Agra and Gurgaon canal respectively. Yamuna enters Delhi near Wazirabad barrage while it leaves at Okhla. The Wazirabad barrage lets out very little water into the river. In summer months especially, the only flow downstream of Wazirabad is of industrial and sewage effluents. Lesser discharge means lesser river flow and thus, greater levels of pollution. From the Okhla barrage, which is the exit point for the river in Delhi, the Agra canal branches out from Yamuna. During the dry months, almost no water is released from this barrage to downstream Yamuna. Instead, discharges from the Shahadra drain join the river downstream of the barrage, bringing effluents from east Delhi and Noida into the river. On the basis of wastewater discharge, Najafgarh drain is the largest drain (contributed by 38 other drains) followed by Shahdara drain and drain near Sarita Vihar Bridge. Moat drain is the smallest drain. (<http://www.cpcb.delhi.nic.in/projresearch>)

**Table 1.2:** Percentage contribution of pollution by Delhi's drains

<b>Drains</b>	<b>% Contribution</b>
Sonepat drain	0.67
Etawah	2.1
Red fort drain	5.9
Shahadra drain	24.31
Tapobhumi drain	1.6
Barapullah drain	4.6
Sen Nursing home drain	7.1
Power house drain	4.8
Civil mill drain	7.2
Najafgarh drain	40.3

Source: CPCB, 1996.

*Chapter II*

*Literature Review*

## LITERATURE REVIEW

As a result of the environmental importance and the heightened awareness about the biochemical and toxicological roles of PAHs in man and animals, these compounds have been studied extensively in different environmental matrixes as sewage, mussels and tap water (Wild et al., 1992; Butler and Sibbald 1986; and Kveseth and Sortland 1982) in particulate matter (Oanh et al., 1999; and Bjorseth, 1977), sediment (Short et al., 1999; and Wilcock et al., 1996) surface runoff (Wust et al., 1992), sea water (Maldonado et al., 1999) and soil .

The widespread distribution of sedimentary PAHs, culprits of carcinogenicity and mutagenicity, has been well documented in industrialized countries, and a vast number of publications are available in the literature. By contrast, only limited sedimentary PAH data have been acquired in recent years from a small range of tropical/subtropical regions in Asia (Zakaria et al., 2002; Maskaoui et al., 2002; Mai et al., 2002; Yuan et al., 2001; Mai et al., 2001; Tam et al., 2001; Zhou et al., 2000; Hong et al., 1995).

To compare concentrations measured at different places around the world, it has to be considered that frequently researchers use different extraction techniques, different analytical tools, and have difference in expertise. This will result in a semi-quantitative comparison at best. Moreover a different suite of PAH molecules are often studied making such comparison even more difficult (Macias-Zamora et al., 2002). So the comparison of total PAH levels from different studies needs to be treated with caution (Maskaoui et al., 2002). In most cases, total PAH concentrations are given as the sum of un-substituted PAH of molecular weights 178 (*Anth*, *Phen*), 202 (*Fl*, *Pyr*), 228 (*B[a]A*, *Chry*), 252 (*BFs*, *B[e]P*, *B[a]P* and *IP*, *B[ghi]P*) (Bouloubassi et al., 2001). However a general estimate figure of the magnitude of the problem can be obtained from these comparisons. So In this sense, the following literature review is for comparative purpose at different sites. (Macias-Zamora et al., 2002)

### 2.1 River sediment

The concentrations of individual PAH in river sediments in 1987-91 varied over a wide range; the maximum values were in the high nanogram per gram range.

The levels of individual PAH in sediments from some of the most polluted areas in continental USA were summarized by Bieri et al. (1986). The levels usually ranged from 1,000 to 10,000  $\mu\text{g}/\text{kg}$ , but that in sediment from the Elizabeth River, Virginia, contained concentrations up to 42,000  $\mu\text{g}/\text{kg}$  . Up to 39,000  $\mu\text{g}/\text{kg}$  wet weights were found in the Detroit River (Fallon & Horvath, 1985).

The concentrations of individual PAH in sediments from the Trenton Channel of the Detroit River, a waterway in a highly industrialized area connecting Lake St Clair with Lake Erie varied from not detected (4  $\mu\text{g}/\text{kg}$ ) to 22,000  $\mu\text{g}/\text{kg}$  in different locations. Sediments from the southwest shore of Grosse Ile had low levels of contamination, while those in the vicinity of Monguagon Creek had high levels (Furlong et al., 1988).

The levels of individual PAH in sediments from German rivers were about 4000 µg/kg for *B(a)P*, *Fl*, and *B(b)F* and about 1500 µg/kg for *Pyr*, *IP*, and *B(a)A*. The levels of other PAH generally did not exceed 500 µg/kg (Krober & Hackl, 1989; Regional Office for Water and Waste Disposal, 1989).

The maximum levels of individual PAH in sediments in Czechoslovakia were 4500 µg/kg *Fl*, 2600 µg/kg *Naph*, 2500 µg/kg *Pyr*, 1500 µg/kg *Chry*, 1000 µg/kg *Anth*, 580 µg/kg *B[ghi]P*, 260 µg/kg *Flu*, 220 µg/kg *Phen*, and 140 µg/kg *Acn* (Holoubek et al., 1990).

Evans et al. (1990) analyzed the freshwater surface sediments from the river Derwent (Derbyshire UK) and total PAHs were found to be in the range from 5.22-352.40 µg/g.

Mai et al. (2002) measured spatial distribution of PAHs in ranges from 1168 to 21,329 ng/g in the riverine sediment samples, whereas the PAH concentration ranges from 323 to 14,812 ng/g in the sediment samples of the Estuary. Sediment samples of the Zhujiang River and Macao harbor around the Estuary show the highest concentrations of PAHs. Possible factors affecting the distribution patterns could be discussed based on the usage history of the chemicals, hydrologic condition, and land erosion due to urbanization processes.

Sanders et al. (2002) analyzed PAHs in surface sediments collected from the Savannah River located in the southeastern state of Georgia, USA. Three sub-divisions of the river were identified for the study: upstream from, adjacent to, and downstream from the city of Savannah. There was high spatial variability in the total PAH ( $\sum$  PAH) concentrations that ranged from 29 to 5,375 ng/g with an average concentration of  $1,216 \pm 1,161$ . Of the three subdivisions, the highest PAH concentrations were in the middle segment, which was adjacent to urban and industrial areas. These pyrogenic PAHs were found to be highly associated with toxicity to benthic organisms. The two-ringed *Naph* and substituted Naphthalenes, which are petroleum-related PAHs, were significantly higher in the lower section of the river relative to the subdivisions. This river segment receives inputs primarily from shipping and boating traffic. *Pery*, which is indicative of non-anthropogenic terrestrial inputs of carbon, had the highest concentration among the individual PAHs measured. High *Pery* concentrations were found at stations located upstream and adjacent to forested terrain and where salinity level was low.

Doong et al. (2004) analyzed the concentrations of 16 PAHs in sediment samples collected from Gao-ping River, Taiwan. The  $\sum$ PAH concentrations in sediments ranged from 8 to 356 ng/g-dry weight with the mean value of  $80.6 \pm 31.8$  ng/g ( $n = 48$ ). Three- and four-ring PAHs including *Phen*, *Anth* and *Pyr* were the dominant species in sediment samples. High contents of PAHs were found in the estuary of the river and in the vicinity of industrial areas.

Zhang et al. (2004) analyzed 16 PAHs in sediment samples from Tonghui River, a typical river in Beijing, People's Republic of China. The total PAHs concentrations ranged from 127.1 -927.7 ng/g, with a mean concentration of 540.4 ng/g. The highest level was found at the site that is located at the mouth of Beiyun River, suggesting sewage discharges from Wenyu River and Tonghui River is important sources of PAHs.

## 2.2 Lake sediment

The concentrations of individual PAH found in Lake Sediments in 1984-91 ranged from 1 to about 30000  $\mu\text{g}/\text{kg}$  dry weight.

The total PAH concentrations in surface sediments from Lake Michigan, USA, were 200-6200  $\mu\text{g}/\text{kg}$  dry weight (Helfrich & Armstrong, 1986).

Khim et al. (1999) analyzed sediment samples from Masan Bay, located on the south-east coast of Korea, for the determination of PAHs. PAHs were predominated by 4-6-ring compounds with concentrations in the range of 54. 1-1100  $\text{ng}/\text{g}$  dry wt.

Surface sediments from Santander Bay, Cantabric Sea, Northern Spain were analyzed and the sum of 16 PAHs was found to range, from 0.02-to 344.6  $\mu\text{g}/\text{g}$  dry wt. A qualitative relationship could be established between the industrial input along the rivers and the concentration of 16PAHs in the sediments of the estuaries: Boo estuary (8404–4631  $\mu\text{g}/\text{g}$  OC), Solia–San Salvador estuaries (305–113  $\mu\text{g}/\text{g}$  OC) and Cubas estuary (31–32  $\mu\text{g}/\text{g}$  OC). This work shows a dramatic change in the spatial distribution in the concentration of PAHs of intertidal surface sediments. The left edge of the Bay has the main traffic around the city and the major source of PAHs is from combustion processes and estuarine inputs, leading to medium values of PAHs in the sediments; the right edge of the Bay has much lesser anthropogenic activities leading to lower values of PAHs in sediments. (Viguri et al., 2002)

The concentrations of 16 polycyclic aromatic hydrocarbons (PAHs), were measured in sediments along the coast of Izmit Bay, the most important bay of the Marmara Sea. The total-PAH concentrations, measured by Spectrofluorometry were in the range of 30.0–1670.0  $\text{mg}/\text{g}$  dry weight in sediments. The most pollution occurred at Dogu Kanali and Dil Deresi where were the main rivers containing wastes fall into the Izmit Bay. (Telli-Karakoc et al., 2002)

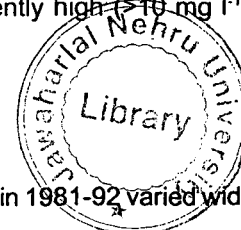
In a study carried out on surface sediments at Todos Santos Bay, Baja California, Mexico. Average PAH concentration was found from 7.6 to 813.0  $\text{ng}/\text{g}$  of dry sediment. The average concentration was found to be 96 $\text{ng}/\text{g}$  (Macías-Zamora et al., 2002)

Zhou et al. (2003) determined the levels of 16 polycyclic aromatic hydrocarbons (PAHs) in sediment samples of the Daya Bay, a key aquaculture area in China. The total concentrations of 16 PAHs varied from 115-to 1134  $\text{ng}/\text{g}$  dry weight with a mean concentration of 481  $\text{ng}/\text{g}$  in sediments. In comparison to many other marine systems studied, the PAH levels in Daya Bay waters were relatively high, and at six sites they were sufficiently high ( $>10 \text{ mg l}^{-1}$ ) to cause acute toxicity.

## 2.3 Estuarine sediments

The concentrations of individual PAH in estuarine sediments in 1981-92 varied widely, with maximum values in the high microgram per gram range.

The total PAH concentrations in sediments from the Penobscot Bay region of the Gulf of Maine, USA, ranged from 290 to 8800  $\mu\text{g}/\text{kg}$ , with a distinct gradient that decreased sea-





wards. The PAH composition was uniform throughout Penobscot Bay. Particulates of combustion products transported in the atmosphere were suggested to be a major source of PAH contamination. The levels in Penobscot Bay sediments were significantly higher than expected for an area previously considered to be uncontaminated and fell within the range found in industrialized regions throughout the world (Johnson et al., 1985).

The levels of PAH in estuarine sediments in the United Kingdom were 10-500  $\mu\text{g}/\text{kg}$ . Higher amounts of Fl (1000-1900  $\mu\text{g}/\text{kg}$ ) and Pyr (790  $\mu\text{g}/\text{kg}$ ) were reported in estuaries of the River Mersey and the River Tamar (Readman et al., 1986).

The concentrations of *B[a]P*, *B[e]P*, *Fl*, *B[b]F*, *B[j]F*, *B[k]F*, *Chry* and triphenylene, *Pyr*, *IP*, *B[a]A*, *DB[a, h]A*, *Pery*, *B[ghi]P*, and *DB[a, e]P* in sediments from the Saguenay Fjord ranged from 2000 to 3800  $\mu\text{g}/\text{kg}$  (dry or wet weight basis not given). The Saguenay Fjord is the major tributary that empties into the St Lawrence River estuary, and the area is highly industrialized. The PAH concentrations were maximal near the aluminum smelting plants that dominate the industrial sector and which were considered to be the major source of PAH, and the levels decreased with distance from this industrial zone. (Martel et al., 1986).

Sedimentary polycyclic aromatic hydrocarbons (PAHs) were studied in the Changjiang Estuary and the adjacent East China Sea. Anthropogenic PAHs originating from combustion/pyrolysis processes varied from 17 to 157 ng/g, while fossil PAH concentrations ranged from 42 to 187 ng/g. Of the studied PAHs, biogenic perylene dominated at stations receiving riverine inputs. Both biogenic and anthropogenic hydrocarbons are primarily derived from riverine discharges and accumulate at shallow-water stations. Fossil PAHs are enhanced at offshore stations where they are introduced directly by shipping activities. Biomarker fingerprints ascribe their source to Chinese crude oils. The overall levels of anthropogenic hydrocarbons are low compared to relevant areas worldwide and reveal a low/moderate level of hydrocarbon pollution (Bouloubassi et al., 2001).

The distribution of 16 polycyclic aromatic hydrocarbons (PAHs) was determined in sediment of the Jiulong River Estuary and Western Xiamen Sea, China. Total PAH concentrations varied from 59–1177 ng/g dry weight in surficial sediments (Maskaoui et al., 2002).

Wu et al. (2003) analyzed selected PAHs in surface sediments of the Yalujiang Estuary, North China, for flood season (August, 1994) and dry season (May, 1996), respectively. PAHs concentrations from sediments range from 68 to 1500 ng/g depending upon the sample locations. The most contaminated sediment samples are found in the turbidity maximum area for both dry and flood seasons. The source of PAHs is most likely pyrolytic, with minor contributions from petrogenic and diagenetic PAHs for some samples. Perylene is mainly derived from biogenic inputs, and occurs at almost stations. In the Yalujiang Estuary, both biogenic and anthropogenic hydrocarbons are primarily derived from riverine discharges and are accumulated in the mixing zone. The overall levels of PAHs in this study were found low compared to other regions and reveal moderate PAHs pollution in the Yalujiang Estuary.

Zhang et al. (2004) analyzed PAHs in surficial sediments, from Minjiang River Estuary, China and found the concentration varying from 112 to 877 ng/g dry wt.

Oros and Ross (2004) examined surface sediments in the San Francisco Estuary for PAH composition over a range of spatial and temporal scales to determine distributions, trends, and possible sources. The mean total PAH (ΣPAH) concentration in sediments was spatially distributed as Central Bay (230 mg/kg TOC), South Bay (217 mg/kg TOC), North Estuary (96 mg/kg TOC), Extreme South Bay (87 mg/kg TOC), and Delta (31 mg/kg TOC).

#### 2.4 Harbor sediment

The levels of individual PAH found in harbor sediments were higher than those in rivers, lakes, or oceans, concentrations < 650 µg/g being reported.

Connell *et al.* (1998b) performed a fate and risk evaluation of some persistent organic chemicals in Victoria harbor, including total PAHs and *B[a]A*. They reported average concentrations for these contaminants within the harbor 387 ng/g and 23.5 ng/g respectively and stated that the risk of biological damage posed by PAHs in Victoria Harbor was difficult to assess. They noted that the Risk Index calculated for *B[a]P* was lower than that for the total PAHs, but was of a value, which still implied the need for further assessment.

Soclo et al. (2000) identified and quantified PAHs in recent sediments of the Cotonou coastal zones (Benin) in the total concentration range 25-1450 ng/g, while the Aquitaine sediment samples (France) exhibited total PAH concentrations in the range 4-855 ng/g.

The concentrations of 16 USEPA priority pollutant PAHs were analyzed in four size fractions (< 62, 62-125, 125-250, and > 250µm) in contaminated Boston Harbor sediments. Total PAH concentrations ranged from 7.3 to 358 µg/g dry wt. and varied largely among the different size fractions in these sediments (Wang et al., 2001).

PAHs concentration (ΣPAHs) in the sediment of Porto Torres Harbor (north Sardinia, Italy) ranged from 0.07 to 1.21 µg/g, indicating low to moderate PAHs pollution (Luca et al., 2004).

#### 2.5 Marine sediments

The concentrations of individual PAH in marine sediments in 1985-91 varied widely, with maximum values up to about 4000 µg/kg.

Maximum levels of 460 µg/kg *B[a]P* and 400 µg/kg *B[e]P* were determined in northern North Sea sediments in the vicinity of oil fields. The hydrocarbon concentrations were above the background levels only in water and sediments within a 2-km radius of platforms, where diesel-coated drill cuttings were dumped. The contribution of five- and six-ring compounds to the total PAH in sediments was unexpectedly high in samples unlikely to be contaminated by oil. Their source was probably windborne combustion products (Massie et al., 1985).

Sediments near power-boat moorings at the coral reef around Green Island, Australia, were found to contain measurable amounts of several PAH, strongly suggesting that they originated from fuel spillage or exhaust emissions (Smith et al. 1987).

Compaan & Laane (1992) analyzed the PAHs in North Sea sediments and found the concentrations as  $< 0.01$ - $20 \mu\text{g}/\text{kg}$  dry weight *B[a]P*,  $< 30 \mu\text{g}/\text{kg}$  *Fl*,  $< 6 \mu\text{g}/\text{kg}$  *B(b)F* plus *B[k]F*,  $< 5 \mu\text{g}/\text{kg}$  *B[ghi]P*, and  $< 3 \mu\text{g}/\text{kg}$  *IP*.

Concentrations of PAHs were measured in recent marine sediments in off the coastal region at the Mexico-USA border. For the PAHs, the average concentration was  $0.4 \mu\text{g}/\text{g}$ , with a maximum of  $1.93 \mu\text{g}/\text{g}$ . The sources of hydrocarbons appeared to be mainly anthropogenic. Distribution of PAHs was found to decrease toward the coast (Macias-Zamora, 1996).

Zheng and Richardson (1999) analyzed surficial sediment samples, obtained from Hong Kong coastal waters for a suite of 15 PAHs. Total PAHs concentration ranged from  $7.25$ - $4420 \text{ ng}/\text{g}$ . The results indicate that Hong Kong coastal sediments are often seriously polluted with petroleum related hydrocarbons. This is especially so in heavily urbanized or industrialized localities, such as Kowloon Bay (Victoria Harbor), Tsing Yi North and Tolo Harbor. Petroleum hydrocarbon pollutants in marine sediments are believed to be mainly derived from the transportation of oil, shipping activities, spillages, and industrial, storm water and wastewater discharge.

Sediment samples, collected from the South China Sea, were analyzed for 11 parent polycyclic aromatic hydrocarbons (PAHs). Total concentrations of the 11 PAHs studied in the sediments ranged from  $24.7$  to  $275.4 \text{ ng}/\text{g}$  with a mean of  $145.9 \text{ ng}/\text{g}$  dry sediment (Yang, 2000).

Liu et al. (2001) determined the concentration of PAHs in surface sediments taken from intertidal flats in the Yangtze estuary and adjacent coastal areas by GC-MS. Total PAH concentration ranged from  $0.263$ - $6.372 \text{ mg}/\text{kg}$  in tidal flat surface sediments. Mean concentration level is  $1.662 \text{ mg}/\text{kg}$ . The concentration levels of total PAHs varied dramatically with in the region. They were found characteristically at maximum near sewage discharge points. Petroleum-derived contamination could be a dominant source in the study area based on the distributions of Flu/Pyr and two and three-ringed and four-ringed congeners in surface sediments, A pyrolytic origin was responsible for higher PAH concentration levels at three sampling sites. The degree of sediment contamination by PAHs in the study area is low to moderate in comparison with other estuarine and tidal flat surface sediments elsewhere.

Magi et al. (2002) studied the distribution of the 16 PAHs in surface sediments of two coastal areas of the Adriatic Sea. Total concentrations of the analytes were detected in the range  $24.1$ - $501.1 \text{ ng}/\text{g}$ .

Basheer et al. (2003) analyzed the concentration of 16 PAH in the sediments from the northeastern and southwestern regions of Singapore's marine waters. The total PAH concentration varied between  $15.22 \mu\text{g}/\text{g}$  and  $82.41 \mu\text{g}/\text{g}$  in the northeastern region and between  $13.63$

$\mu\text{g/g}$  and  $84.92 \mu\text{g/g}$  in the southwestern region. The highest concentration of total PAH i. e.  $84.92 \mu\text{g/g}$  was recorded at a site adjacent to a petrochemical refinery. Among the sixteen individual PAHs, *Chry*, *IP* and *B[a]A* were most prevalent in the sediments. A comparison of total PAH concentration data for sediments collected from Singapore relative to those reported for other countries indicates a moderate level of PAH contamination in Singapore's coastal marine sediments.

Total concentrations of PAHs in Singapore's coastal marine sediments (i. e.  $93.85 \mu\text{g/g}$ ) are comparatively lower than that reported for sediments from Kitimat Harbor, Canada (i. e. up to  $10,000 \mu\text{g/g}$  (Simpson *et al.*, 1996)); Times Beach, New York, U. S. A. (i. e. up to  $480 \mu\text{g/g}$  (Roper and Chery, 1994)); Santander Bay, Spain (i. e. up to  $344.6 \mu\text{g/g}$  (Viguri *et al.*, 2002)); Harbor of Refuge, Rhode Island Sound, U. S. A. (i. e. up to  $730.0 \mu\text{g/g}$  (Ho *et al.*, 1999)); Sydney harbor, Australia (i. e. up to  $380 \mu\text{g/g}$  (McCready *et al.*, 2000)); Kohtla-Järve, Estonia (i. e. up to  $153.0 \mu\text{g/g}$  (Trapido, 1999)), but higher than that reported for sediments in the Mediterranean Sea (i. e. up to  $20.50 \mu\text{g/g}$  (Baumard *et al.*, 1998)); Pacific Coast, USA (i. e. up to  $20 \mu\text{g/g}$  (Brown *et al.*, 1998)); Arkona Basin, Baltic Sea, Germany (i. e. up to  $1.80 \mu\text{g/g}$  (Witt, 1995)); and the Barents Sea, Svalbard, Norway (i. e. up to  $2.00 \mu\text{g/g}$  (Stange and Klungsøyr, 1997)); and Mai Po, Hong Kong (i. e. up to  $0.96 \mu\text{g/g}$  (Gene *et al.*, 2002).

Mai *et al.* (2003) analyzed PAHs in the Coastal Region off Macao, China and found that the total sediment PAHs concentrations ranged from 294 to  $12,741 \text{ ng/g}$ , categorized as moderate contamination compared to other regions of Asia and the world. In addition, the PAH compounds appeared to be bound more strongly to aromatics-rich soot particles than to natural organic matter, implying a prevailing atmospheric transport route for PAHs to Macao's coast.

In general, PAH concentrations in sediments of Macao's coastal region and the rest of the Pearl River Delta were lower than or comparable to those in Tokyo Bay ( $534\text{-}292\text{ }370 \text{ ng/g}$ ), higher than those in riverine and coastal sediments of Malaysia ( $4\text{-}924 \text{ ng/g}$ ), and well around the midpoint of the global PAH concentration range (Zakaria, *et al.*, 2002).

Ogunfowokan *et al.* (2003) investigated distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments of Lagos, Osogbo and Ile-Ife Western areas of Nigeria by Gas Chromatography-Mass spectrometry (GC-MS) technique. PAHs in sediment of Lagos contribute an average of  $228.57 \text{ mg/kg}$  PAH to the total sediment PAH burden compared to Osogbo and Ile-Ife areas that contribute only  $91.13 \text{ mg/kg}$  average PAH to the total PAH burden of the study area.

## **2.6 Role of organic carbon and association of PAHs in different size fraction**

The distribution of PAHs in sediments is often described by their partitioning between different phases. Numerous studies have been conducted to determine the partitioning of PAHs in sediments (Karickhoff *et al.*, 1979; Means *et al.*, 1980; Chin and Gschwend, 1992; Maruya *et al.*, 1996; Chiou *et al.*, 1998; Kleinedam *et al.*, 1999). In all these studies organic matter

content of aquatic sediments has been shown to be very important in terms of complexing hydrophobic toxic pollutants. (Wang et al., 2001). Dissolved organic material (DOM) has been shown to complex certain Polycyclic aromatic hydrocarbons (PAH's), rendering them unavailable for uptake into aquatic organisms (Leversee et al., 1983; Landrum et al., 1985; McCarthy and Jimenez, 1985; McCarthy et al., 1985). The degree of hydrophobicity of the pollutant affects the proportion of the compound bound to DOM or conversely the amount of DOM which is required to bind all of the contaminant present in the system (Evans et al., 1990).

Partitioning of organic contaminants between the two phases has also been correlated with clay content of the sediment (Karickhoff and Brown, 1978; O'Conner and Connolly, 1980) where highest partitioning has been reported to occur in the clay fraction, This effect has been related to the efficiency of exchange sites and the organic matter associated with this size fraction (Evans et al., 1990).

The importance of sedimentary organic matter or the partitioning of PAHs in sediments has been well documented in both laboratory adsorption experiments and field studies (Karickhoff et al., 1979; Means et al., 1980; McGroddy and Farrington, 1995). By using solid-state  $^{13}\text{C}$  studies, Chiou et al. (1998) found that the high partitioning of PAHs to sedimentary organic matter was mainly due to the significant aromatic fraction of the organic matter. They considered the sedimentary organic matter as a natural "heterogeneous polymer" where PAHs interact more favorably with the aromatic regions. Particulate organic matter of charcoal, plant detritus and coal particles sorbed Phen most strongly ( $\log K_{oc} = 6.3-6.7$ ), while organic matter adsorbed onto clay mineral surfaces with high maturation had less sorption of Phen ( $\log K_{oc} < 4.7$ ).

Few studies have investigated the association of PAHs in different size fractions in sediments (Prahl and Carpenter, 1983; Boehm and Farrington, 1984; Evans et al., 1990;). Prahl and Carpenter (1983) found that PAHs were selectively associated with low density, large particle size fractions which comprised mainly vascular plant and pieces of charcoal in coastal sediments near Washington State. Similarly, Simpson et al. (1998) found that in the highly contaminated Kitimat Harbor in British Columbia, high PAH concentrations were associated with large size fractions (300-1180 and  $> 1180\mu\text{m}$ ), which contained high particulate organic matter of charcoal, plant detritus and coal particles. Wang et al. (2001) found that the highest PAH concentrations were associated with the large size ( $> 250\mu\text{m}$ ) fractions while the fine silt and clay fractions ( $< 62\mu\text{m}$ ) contained relatively low PAHs. Despite the great concentration differences, the composition of PAHs in the four size fractions of these sediments showed similar patterns dominated by PAHs with three or more rings.

Maruya et al. (1996) reported that in sediments collected from San Francisco Bay, high PAHs were mainly associated with silt and clay fractions and sedimentary organic matter had less effect on the distribution of PAHs in the sediments. Kim et al. (1999) observed a positive correlation between PAHs and sedimentary organic matter, but negative correlation

between PAHs and sediment grain size in the sediments collected from Kyeonggi Bay, Korea.

There have been conflicting reports on the relationships between organic pollutants and sediment particle sizes. Umlauf and Bierl (1978) reported a PAH maximum in the middle silt range (12.5 to 20  $\mu\text{m}$ ) followed by the fine and coarse silt fractions (6.3 to 12.5  $\mu\text{m}$  and 20 to 63  $\mu\text{m}$ ) and Boehm and Farrington (1984) found a direct positive relationship between PAH content and silt/clay content of recent sediments. Other workers studying PAHs and other organic pollutants have also found a tendency for the pollutant in question to be associated with the silt and clay fractions (Lotse et al., 1968; Choi and Chen, 1976; Zuofeng, 1987). However, Readman et al. (1984) found a decrease in PAH content of estuarine sediment with decreasing particle size from sand to clay (100 to 10  $\mu\text{m}$ ) and Hoffman et al. (1984) stated PAH's attached to particulates in storm water had maxima in the 125 to 250  $\mu\text{m}$  and 45  $\mu\text{m}$  particle sizes (Evans et al., 1990).

Evans et al. (1990) investigated the relationship of PAHs with organic matter present in various river sediment size fractions, from 63  $\mu\text{m}$  to 1.0 to 2.0 mm and found that the PAH and organic matter content have bimodal distributions through the sediment size fractions which may be explained by the presence of two types of organic material in the sediment.

## 2.7 Source Signatures

Parent and alkyl-substituted PAHs have both natural sources (oil seeps, bitumens, coal, plant debris, forest and prairie fires) and anthropogenic sources (fossil fuels and combustion). Since the PAH compositions of the two sources overlap, especially for parent PAHs, the significance of anthropogenic PAH in the environment must be evaluated against a dynamic background of natural PAH. Parent and alkyl-substituted PAHs provide some of the most definitive and ubiquitous tracers of organic matter in aquatic systems (e.g. Bouloubassi and Saliot, 1993; Yunker et al., 1993, 1999; Budzinski et al., 1997; Fernandes and Sicre, 1999). Despite this widespread applicability of PAHs, most studies have been limited to a specific location or type of sample, with the result that few studies have comprehensively addressed the relative suitability of various commonly applied PAH ratios as indicators.

### 2.7.1 The use of PAH ratios to infer source

The PAH composition at a given point in the environment reflects the source from which the PAHs were derived; however this "source signature" will be altered by environmental processes which act selectively or differentially on individual PAHs. Changes in PAH composition as a function of sediment particle size has been attributed to different source inputs (Prah and Carpenter, 1983) or differential partitioning among particle size classes (Maruya et al., 1996; Kukkonen and Landrum, 1996).

The characteristics of different PAH sources and the changes in PAH composition between source and sediment (the relative stability of different PAH isomers and PAHs from

different sources).

### 2.7.2 Parent PAH relative stability

Parent PAH ratios have been widely used to detect combustion-derived PAH (Lipiatou and Saliot, 1991; Benner et al., 1995; Yunker et al., 1996, 1999; Budzinski et al., 1997). To minimize confounding factors such as differences in volatility, water solubility, adsorption, etc., ratio calculations usually are restricted to PAHs within a given molecular mass (Readman et al., 1987; McVeety and Hites, 1988). For parent PAHs, combustion and/or anthropogenic input is often inferred from an increase in the proportion of the less stable, kinetic PAH isomers relative to the more stable, thermodynamic isomers (Yunker and Macdonald, 1995) and the stability of the lighter PAH isomers has been calculated to support such interpretations (Budzinski et al., 1997, and references therein).

Based on thermodynamic calculations, the formation of structural isomers such as *Phen* and *Anth* that occurs at low temperature (300°K), such as during the slow maturation of petroleum, is kinetically controlled. These molecular formations are governed by the thermochemical stability of each molecular structure, with the most stable structure having the higher molar fraction. *Phen* is more thermo-chemically stable than *Anth*, and therefore at low maturation temperatures much higher molar fraction of *Phen* is produced compared to *Anth* (Alberty and Reif 1988). To the contrary, at high-temperature processes, the relative stabilities are controlled by the entropy of formation (Alberty and Reif 1988). Thus, the mole fractions become more uniform as the temperature is increased.

Likewise, discrimination also occurs in the *Fl*/202 ratio. In petroleum-derived PAHs, *Pyr* is more abundant than *Flan*. At higher combustion temperatures a predominance of *Fl* over *Pyr* is characteristic.

This implies that the mass 178 and 202 isomers have the greatest range in stability and hence good promise as indicators of thermodynamic vs. kinetic (e.g. petroleum vs. combustion) sources, whereas masses 278 and 228 show little promise as such indicators.

### 2.7.3 PAH source characteristics

PAHs of molecular mass 178 and 202 are commonly used to distinguish between combustion and petroleum sources (Budzinski et al., 1997; Soclo et al., 2000). For mass 178, an *Anth* / *Anth* + *Phen* (*Anth*/178) ratio < 0.10 usually is taken as an indication of petroleum while a ratio > 0.10 indicates a dominance of combustion (Budzinski et al., 1997). High temperature processes such as the carbonization of bituminous coal to form creosote (Goyette and Brooks, 1998) have PAH ratios similar to coal tar or coal combustion and generally are indistinguishable from combustion. Accordingly, the *An*/178 boundary of 0.10 appears generally applicable with the caveat that ratios > 0.10 for diesel oil, shale oil, coal and some crude oil samples and < 0.10 for lignite, diesel and No. 2 fuel oil emissions have been reported.

For mass 202 a  $Fl/Fl+Pyr$  ratio of 0.50 is usually defined as the petroleum/combustion transition point (Budzinski et al., 1997), but in practice this boundary appears to be less definitive than 0.10 for *Anth/178*. The  $Fl/Fl+Py$  ratio is below 0.50 for most petroleum samples and above 0.50 in kerosene, grass, most coal and wood combustion samples and creosote, but is below 0.50 for gasoline, diesel, fuel oil and crude oil combustion and emissions from cars and diesel trucks. Crude oil samples from most studies have ratios  $<0.40$ , but the mean ratio for Australian crude oils is  $>0.40$ , and a few oils have very high proportions of *Flan*. Vehicle and crude oil combustion particulates are more uniform (0.41–0.49) and closer to the 0.50 boundary than diesel exhaust (particulate plus vapor 0.20–0.58), suggesting that unburned diesel depresses the *Flan*, proportion in exhaust samples (Sjogren et al., 1996; Schauer et al., 1999; Wang et al., 1999). Further complicating the use of mass 202 ratios, the PAH composition can differ between diesel fuels or between the vapor and particulate phases for diesel and crude-oil emissions (Benner et al., 1990; Schauer et al., 1999; Westerholm et al., 2001). Overall, however, the petroleum boundary ratio appears closer to 0.40 than 0.50 for  $Fl/Fl+Py$  and ratios between 0.40 and 0.50 are more characteristic of liquid fossil fuel (vehicle and crude oil) combustion whereas ratios  $>0.50$  are characteristic of grass, wood or coal combustion.

PAHs of molecular masses 228 and 276 are used less frequently as parent PAH indicators and few guidelines have been established for their interpretation (e.g. Gogou et al., 1996; Yunker et al., 1996, 1999). The higher mass PAHs usually are minor contributors to refined petroleum products (Wang et al., 1999) and generally are present in significant amounts only in higher fractions such as asphalt (Readman et al., 1987), and possibly in bitumen or coal. Hence, the large variation in petroleum composition for both  $B[a]A$  to  $B[a]A + Chry/triphenylene$  ( $B[a]A/228$ ) and  $IP/IP + B[ghi]P$  likely is a combination of heterogeneous samples and analytical variability due to low concentrations. Because very low proportions of  $B[a]A$  or  $IP$  are rarely observed in combustion samples, a  $BaA/228$  or  $IP/IP+Bghi$  ratio less than about 0.20 likely indicates petroleum. Ratios of  $B[a]A/228$  and  $IP/IP+Bghi$  for suspended particulate and sediment samples from the Mackenzie River delta and shelf ( $0.14 \pm 0.03$  and  $0.15 \pm 0.03$ , respectively; mean  $\pm$  SE,  $n=79$ )—where PAHs have a natural, petroleum-related source (Yunker et al., 1993; Yunker and Macdonald, 1995)—support this inference.

A  $B[a]A/228$  ratio over 0.50 has been taken to indicate combustion while a ratio below 0.50 has been attributed to low temperature diagenesis (Soclo et al., 2000). The literature review suggest that 0.50 is probably too high for the diagenesis/combustion transition, and that  $B[a]A/228$  ratios  $<0.20$  imply petroleum, from 0.20 to 0.35 indicate either petroleum or combustion, and  $>0.35$  imply combustion.

Literature values of the  $IP/IP+B[ghi]P$  ratio are above 0.50 for grass combustion, wood soot, creosote, almost all wood and coal combustion aerosols and a bush fire, but are below 0.50 for a savanna fire. In contrast, combustion products of gasoline, kerosene, diesel and crude oil all have ratios below 0.50, with vehicle emissions falling between 0.24 and 0.40. The



higher mass PAHs are appreciable constituents in samples of wood soot (Li and Kamens, 1993), but are only marginally detectable in wood smoke and aerosol (Jenkins et al., 1996; Fine et al., 2001; Schauer et al., 2001), hence the  $IP/IP+B[ghi]P$  ratios for wood soot are likely to be more representative of material that is accumulating in sediments. Accordingly,  $IP/IP+B[ghi]P$  ratios  $<0.20$  likely imply petroleum, between 0.20 and 0.50 liquid fossil fuel (vehicle and crude oil) combustion, and ratios  $>0.50$  imply grass, wood and coal combustion.

The data in literature suggest that PAHs with four and more rings (mass 202 and higher) do not allow a simple segregation into combustion or petroleum sources and that the PAH ratio interpretations are most definitive for masses 202 and 276—the PAHs with largest differences in thermodynamic stability between isomers. Mass 178 and 228 PAHs have much smaller energy differences between isomers and their respective ratios appear to be less responsive to differences in petroleum or combustion source.

#### 2.7.4 PAH composition stability

Because some PAH react faster than others in atmospheric chemical processes, PAH ratios in the atmosphere often will depart from those seen in source emissions (Schauer et al., 1996; Fraser et al., 1998b). Various studies have demonstrated that  $B[a]P$ ,  $B[a]A$  and Anth degrade photolytically in the atmosphere at much faster rates than their isomers or other commonly-measured parent PAH (e.g. Kamens et al., 1986, 1988; Masclet et al., 1986; Behymer and Hites, 1988). In Mediterranean aerosol the most photoreactive components (typically  $B[a]A$  and  $B[a]P$ ) show depletion between urban and remote areas for PAHs that have a primary source in vehicle emissions (Sicre et al., 1987; Gogou et al., 1996; Tolosa et al., 1996). Ambient air data for Los Angeles demonstrate that Anth proportions are lowest in daytime and indicate that Anth undergoes more rapid photochemical reaction in the atmosphere than Phen (Fraser et al., 1998b). In contrast, the Fl/Pyr and  $IP/B[ghi]P$  isomer pairs degrade photolytically at comparable rates (Masclet et al., 1986; Behymer and Hites, 1988), suggesting that the original composition information is preserved during atmospheric transport.

Biomass and fossil fuel combustion processes produce aerosols with very different particle sizes and physical properties (Schmidt and Noack, 2000; Gelinas et al., 2001). These differences affect both the dispersion pathways in the environment and the physical protection afforded combustion products such as the PAHs (Gelinas et al., 2001).

Black carbon forms in two fundamentally different ways (Schmidt and Noack, 2000). Char (and charcoal) black carbon forms during the flaming and smouldering of the cellulose-rich (Nolte et al., 2001) solid residues of plant tissues and is a common product of wildfires. In contrast, soot black carbon is generated from volatiles formed within flames and subsequently re-condensed by free radical reactions to form the graphite-rich material that is more typical of fossil fuel combustion. The char and soot black carbon forms follow different distribution pathways in the environment and vary in their chemical and physical properties (Gelinas et al.,

2001, and references therein). Because soot black carbon is formed in the phase-phase and has a smaller mean size than residual particles of charred biomass, it is rapidly dispersed through aerosol formation and atmospheric transport and deposition. In contrast, the larger particles of char black carbon tend to accumulate in soils close to source and primarily are transported by surface runoff and rivers to lake or continental margin sediments (Gelinás et al., 2001).

Pyrogenic PAH generally associate with soot-rich particles that protect them from degradation in the atmosphere, water column and sediments (Behymer and Hites, 1988; Baker et al., 1991; Tolosa et al., 1996; Simo et al., 1997). Greater protection would be expected with a larger particle size or with the encapsulation of PAHs within a particle, rather than adsorption on the surface. The amount of protection also is dependent on the particle color, because PAHs associated with light colored or grey substrates photodegrade much faster than PAHs associated with dark colored or black substrates (Behymer and Hites, 1988). Because the char black carbon of wood soot consists of large, dark, refractory particles (Schmidt and Noack, 2000) that provide a solid matrix that traps and stabilises PAH (cf. Rogge et al., 1998), a recognisable PAH fingerprint of combustion can survive over geological time scales (Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Jiang et al., 1998). Accordingly, it is likely that char from wildfires affords much greater protection towards photolysis than is observed for carbon black or other black soot from fossil fuel combustion (Behymer and Hites, 1988).

Doong et al. (2004) utilized the ratios of specific PAH compounds including *Phe/Anth*, *FL/Pyr*, *Chry/B[a]A*, low-molecular-weight PAH/high-molecular-weight PAH (LPAH/HPAH) to evaluate the possible sources of PAH contamination in Gao-ping River, Taiwan. These ratios reflect a mixed pattern of pyrolytic and petrogenic inputs of PAHs. The petrogenic PAHs may be mainly from the leakage of crude oil and the refined products from urban vehicle traffic, while the pyrolytic PAH input is located in the proximity near the mouth of estuary of the River. The PCA analysis confirmed that petrochemical industrial parks located in the vicinity of estuary of Gao-ping River might be the possible source for the PAH input.

## **2.8 Preparation of sample for PAHs analysis**

A homogenization of the material (e.g., some foodstuffs, soil, sediment, tissues, plants) is normally required before a sample is extracted.

### **2.8.1 Extraction**

Most environmental samples contain small amounts of PAHs, requiring sophisticated techniques for detection and quantification.

Therefore, it is essential to perform an efficient extraction from the sample matrix, followed by one or more purification steps enabling the sample to be analyzed as much as possible free from impurities and interferences. A very large number of extraction and purifica-

tion techniques, as well as of their combinations ('isolation schemes'), are described in the literature. Also considering one specific matrix, there is no single scheme commonly recognized as 'the best', although various methods have been validated and recommended.

The available techniques have been reviewed (Lee et al., 1981; Santodonato et al., 1981; Grimmer, 1983), particularly the extraction methods (Griest & Caton, 1983): in very general terms, depending on the matrix, PAHs are extracted from the sample by a Soxhlet apparatus (e.g., filters loaded with particulate matter or vehicle exhausts, sediments), or directly by liquid-liquid partition (water samples), or - after complete sample dissolution (e.g., fats, vegetable and mineral oils) or alkaline digestion (e.g., meat products) - by a selective solvent such as N,N-dimethylformamide or (Natusch & Tomkins, 1978) dimethylsulfoxide. The complete PAH extraction from samples such as soot emitted by diesel engines, carbon blacks, and other carbonaceous materials is particularly difficult.

As an alternative to Soxhlet extraction, particularly from solid samples and filters loaded with particulate matter, ultrasonic extraction (review by Griest & Caton, 1983) is becoming more and more successful for the advantages in terms of reduced time of extraction (minutes versus hours), with recovery efficiencies and reproducibilities, which may also be superior. There is not a generally valid conclusion regarding which technique is most favorable since the results of a comparison depend on matrix, solvent and experimental conditions.

Recently, supercritical fluid extraction (SFE) (Langenfeld et al., 1993) has gained attention as a rapid alternative to conventional liquid extraction from PUF sorbents (Hawthorne et al., 1989a), soil (Wenclawiak et al., 1992), and other environmental solids such as urban dust, fly ash, and sediment (Hawthorne & Miller, 1987). SFE may also be directly coupled with on-column GC the extract is quantitatively transferred into the GC column, yielding rapid (less than 1 h) analysis with maximum sensitivity. This technique has been applied to urban dust samples (Hawthorn et al., 1989b).

### **2.8.2 Clean-up**

Purification of extracted samples from other classes of interfering substances is most commonly accomplished by adsorption column chromatography. The classical sorbents, alumina and especially silica gel, are widely used. In addition, the hydrophobic Sephadex LH-20 has been found to be suitable to isolate PAHs from nonaromatic, nonpolar compounds (which is important if the sample is analyzed by GC) (Grimmer & Bonke, 1979b), and - in partition chromatography, as a carrier of the stationary phase - to separate PAHs from alkyl derivatives (Grimmer & Banke, 1979a). Chromatographies on silica gel and Sephadex are often combined (Jacob & Grimmer, 1979; Grimmer, 1983). Clean-up has been performed also by eluting extracted samples through XAD-2 (soil samples: Spitzer & Kuwatsuka, 1986), or XAD-2 and Sephadex LH-20 in series (foods: Vaessen et al., 1988), or Florisil columns (food, water and

sediment samples).

Conventional chromatographic columns may be substituted with pre-packed commercial cartridges, with advantages in terms of time and solvents consumed, and of reproducibility performance. For example, silica cartridges have been used in purification of foodstuffs (Dennis et al., 1983), urine (Becher & Bjorseth, 1983), vehicle emissions (Benner et al., 1989), mineral oil mist (Menichini et al., 1990), and atmospheric samples (Baek et al., 1992); soil samples have been cleaned up through Florosil cartridges (Jones et al., 1989).

Alternatively to chromatography on silica gel columns, preparative thin-layer chromatography is also used, e.g., with air particulates and vegetable oils (Menichini et al., 1991).

To avoid photodecomposition of PAHs, sample handling in the absence of UV light is recommended at any stage, and particularly during adsorption on chromatographic media. To avoid significant losses of more volatile PAHs, samples do not have to be evaporated to dryness. Other generally recommended precautions are: to control possible sources of contamination (particularly, from solvents), to store samples - at all stages - refrigerated and in the dark, to keep the water bath temperature of the rotary evaporator under about 35-40°C.

## 2.9 Analytical methods

Hundreds of publications have described analytical methods for PAHs. Table 2.5, systematically presents a limited number of methods applied to 'real' samples of different matrices, taken as examples. The methods and sources were selected, as far as possible, according to the following criteria: accessibility of the bibliographic source, completeness of the procedure description (or including reference to other accessible sources), practicability with common equipment for this type of analysis (even if requiring experienced personnel), recency, status of official or validated or recommended method. For selecting the appropriate method reference is made to many reviews and research paper (Furton et al., 1993; Gadzala and Buszewski, 1995).

At present, identification and quantification of PAHs are routinely performed by gas chromatography (GC) or high-performance liquid chromatography (HPLC). Each technique presents a number of advantages over the other one. Both of them are rather expensive, particularly HPLC, and require qualified operating personnel. Nevertheless, they are deemed necessary to analyse 'real' samples for a large number of PAHs with accuracy and precision.

Reference materials of certified higher than 99% purity are available for 22 of the PAHs considered (BCR, 1992); the remaining compounds are commercially available as chemical standards. with purities of 99% or higher.

### 2.9.1 Thin-layer chromatography

Nowadays, thin-layer chromatography (TLC) is commonly limited to the identification of individual compounds (namely, BaP), particularly for screening purposes (IUPAC, 1987), or

of selected PAHs such as the six PAHs (Borneff and Kunte, 1979) whose determination was recommended by the WHO (1971) in drinking water. Indeed, it is an inexpensive and quick analytical technique, but with low separation efficiency.

Quantification may be performed by spectrophotometric or spectrofluorimetric methods in solution after extracting the scrubbed substance spot (Howard, 1979; also reported in AOAC, 1990), or in situ by scanning spectrofluorimetry (Borneff and Kunte, 1979).

### **2.9.2 Gas chromatography**

Excellent separation capacities (about 3000 and more plates per meter) are obtained by fused silica capillary columns, which are commercially available. This makes it possible to analyse very complex mixtures containing over one hundred PAHs.

The most widely used stationary phases are the methylpolysiloxanes: especially SE-54 (5% Phenyl, 1% vinyl- substituted) and SE-52 (5% phenyl-), but also SE-30 and OV-101 (unsubstituted), OV-17 (50% phenyl-), Dexsil 300 (carborane-), as well as their equivalent phases. The use of chemically bonded phases is increasing because of the advantages in terms of rinsability to restore column performance and lower bleeding at the high temperatures of analysis (about 300 °C) that are required for analyzing the high-boiling compounds.

Splitless or on-column injections are necessary to gain sensitivity in trace analysis, the latter being preferred as it allows better reproducibility. A flame ionization detector (FID) is almost universally employed because of its excellent response linearity, sensitivity and reliability. Since the FID signal is related linearly to the carbon mass of the compound, PAHs are recorded in proportion to their quantities and the chromatogram directly represents the quantitative composition of the sample. Because of the non-selectivity of FID, samples for GC need to be highly purified from interference. Peak identification, which is routinely performed by means of retention data, has to be confirmed by analyzing the sample with a different GC column or by an independent technique, such as HPLC, or by a mass spectrometric (MS) detector directly coupled to the gas chromatograph (GC-MS).

MS detectors have gained wide acceptance. They are powerful tools in identifying compounds, especially when the commercially available libraries of reference spectra are used to match the spectra obtained and control the compound purity. However, isomeric compounds often exhibit indistinguishable spectra, so that the final assignment must also rely upon retention data.

For analysis of PAHs GC-MS has been used widely (McCready et al., 2000; Liu et al., 2000; Mai et al., 2001; Mai et al., 2003; Wu et al., 2003; Basheer et al., 2003; Luca et al., 2004; Doong and Lin, 2004; Oros and Ross, 2004; Zhang et al., 2004)

An on-line coupling of liquid chromatography (LC), capillary GC and quadrupole MS has been performed in determining PAHs in vegetable oils (Vreuls et al., 1991).

### 2.9.3 High-Performance Liquid Chromatography

The packing material considered the most suitable for PAH separation consists of silica particles chemically bonded to linear C<sub>18</sub> hydrocarbon chains. Typically, 25-cm columns packed with 5- $\mu$ m particles are used with the gradient elution technique, and the mobile phase consists of mixtures of acetonitrile/water or methanol/water ('reversed-phase HPLC'). The separation efficiency, which can be achieved with HPLC columns, is quite lower than in capillary GC, which makes HPLC generally less suitable for samples containing complex PAH mixtures.

On the other hand, relevant advantages of HPLC derive from the capabilities of the detectors. Those most widely used for PAHs are ultraviolet (UV) and fluorescence detectors, generally arranged in series, employing flow-cell photometers or spectrophotometers. Both of them, and especially the latter, are high specific and sensitive (the detection limits in fluorescence are at least one order of magnitude lower than in UV). Specificity of fluorescence detector allows for the determination of individual PAHs in the presence of other non-fluorescing substances. In addition, since different PAHs have different absorptivities or different fluorescence spectral characteristics at given wavelengths, the detectors can be optimized for maximum response for specific compounds; in particular, this may prove advantageous in the identification of unresolved components. HPLC is not suitable for lower-molecular mass compounds (namely, Naphthalene, Acenaphthylene, and Acenaphthene), which have relatively high detection limits (US EPA, 1984).

In addition, owing to the selectivity of packing materials, various isomers which cannot be separated, or only partially so, by usual capillary columns, are baseline resolved and identified by HPLC, e.g. the pairs Chrysene-Triacene, and Benzo(b)fluoranthene-Benzo(k)fluoranthene (Wise et al., 1980).

The coupling of an MS detector to HPLC has been developed and also applied to PAH detection (e.g., Quilliam and Sim, 1988).

For applications of HPLC to PAHs, reference is made to published papers and reviews (Sanders et al., 2002; Pandey et al., 1999; Wise 1983, 1985).

### 2.9.4 Other techniques

A number of non-conventional instruments and techniques, based on spectroscopic principles, have been - and still are being - developed as possible alternatives to the chromatographic methods for PAHs. However, most of them are quite expensive, require skilled personnel, and are not yet considered useful for the practicing analyst. For details on such techniques and their applications to PAHs, reference is made to published reviews (Wehry, 1983; Vo-Dinh, 1989). Low-temperature luminescence in frozen solutions ("Shpol'skii effect") has been applied to various environmental samples, particularly to identify methylated PAH isomers (Garrigues and Ewald, 1987; Saber et al., 1987). Synchronous luminescence and room temperature

phosphorimetry have been reported as simple and cost-effective screening techniques for PAHs (Vo-Dinh et al., 1984; Abbott et al., 1986).

Infrared analysis - and particularly Fourier transform infrared (FTIR) spectroscopy coupled to GC (Stout and Mamantov, 1989), and capillary supercritical fluid chromatography (SFC) (Wright and Smith, 1989) have also been applied to PAHs.

## *Chapter III*

### *Materials and Method*



## MATERIAL AND METHODS

Sediment samples were collected during three seasons viz. Pre-monsoon (June 2003), Monsoon (July 2003) and Post Monsoon (September 2003) from the bank of river Yamuna at five locations (Fig 3.1).

### 3.1 Sampling sites

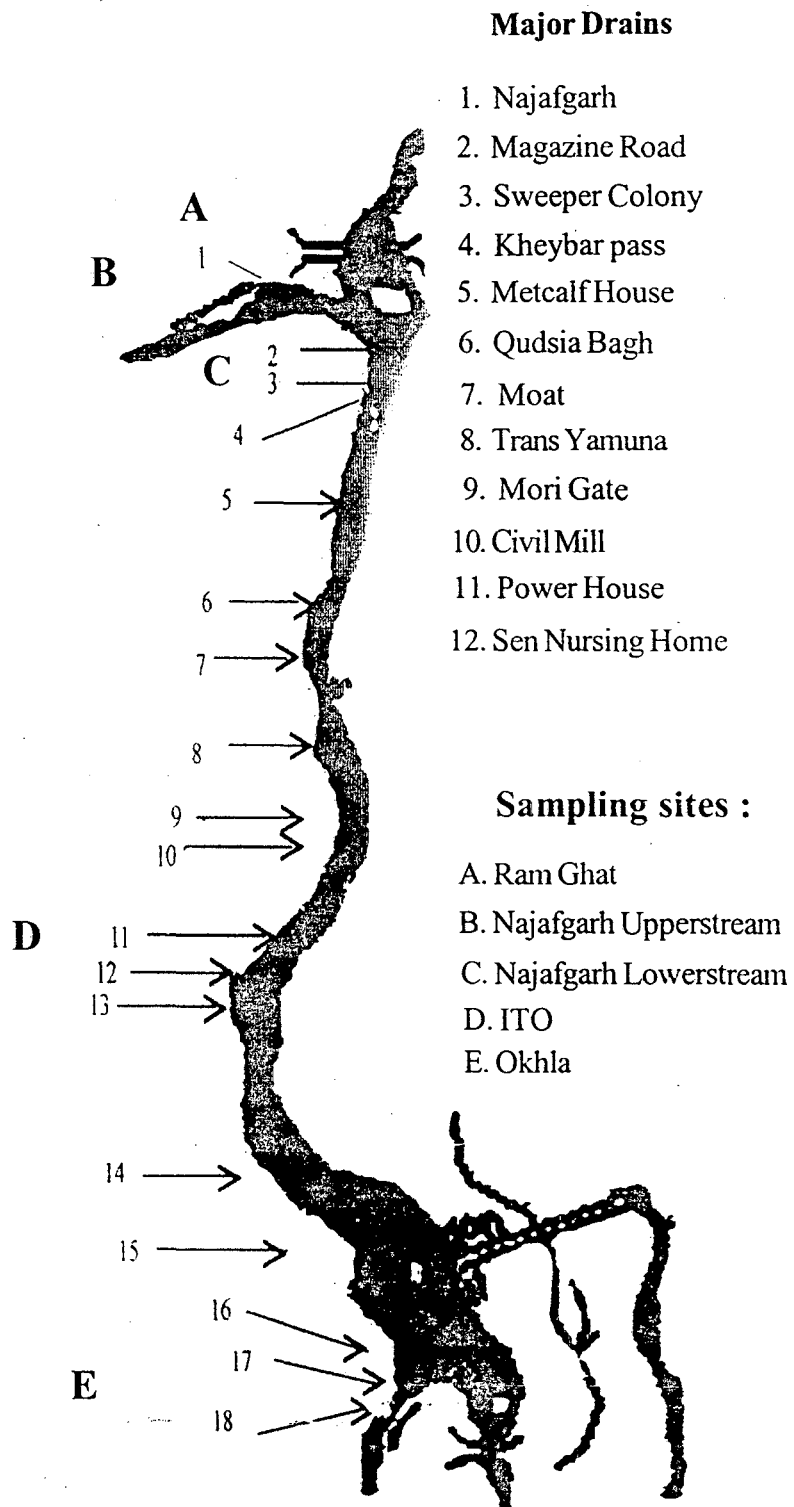
The following sampling sites were chosen on the basis of effluent discharge points.

1. **Ramghat (RG):** Along the course of river Yamuna, near entry point, we chose this sampling location as the first. Ramghat is in Wazirabad district in the north Delhi. This site does not have high industrial setups in close vicinity and hence the contribution of pollutants is only through the domestic and agricultural wastes.
2. **Najafgarh drain (Upstream) (NGUS):** This is second water sampling site around 2 km down of Ramghat.
3. **Najafgarh drain (Down stream) (NGDS):** This is sampling site after the Najafgarh *nala* opens into the Yamuna. Here the river is not as deep as it is at upstream of *nala*. The river flow is very slow. The sampling site is about half a kilometer from the entry point of the *Nala* at river.
4. **Income Tax office (ITO):** Here the Yamuna is very wide and also deep. Its water seems to be dark. The Rajghat thermal power station is at a distance of 2-3 km. This point is around 4-5 km from the previous sampling site.
5. **Okhla (OK):** This sampling site is around 5-6 km from the previous sampling point down the river. Between ITO and Okhla is situated the Indraprastha Thermal Power Station, Barapullah Drain, Hindon cut canal and Shahdra drain which all contribute to Okhla reservoir. The sampling point is just out skirt to the Okhla reservoir around half a kilometer down.

### 3.2 Sample collection and preparation

The surface sediments (1-5 cm) were collected by metal paddle from the river-bank, where the water current were touching the bank, transferred into a polythene bags and transported

**Fig 3.1:** River Yamuna stretch in Delhi showing sampling sites and major drains



to labs. Three spots were chosen at each sites within a distance of 1Km. Thus at each site a set of three samples were collected. In the lab the samples were dried in dark, twigs and stones were removed. Then samples were homogenized and were sieved to include sediments of size range from 0-53  $\mu\text{m}$ . After sieving samples in triplicates were mixed thoroughly to make a composite sample.

### **3.3 Sample extraction and fractionation**

Recent works (Song et al., 2002; Sun et al., 1998; Marvin et al., 1992) report that ultrasonic methods are best suited for the extraction of PAHs from sediments and soils as compared to soxhlet extraction where long time is consumed. Therefore, sediment samples were extracted by ultra-sonication, a method developed and verified by the various authors (Hong et al., 1995; Zhou et al., 2000). Sediment samples (approximately 5-g dry weight) were extracted in 50 ml of toluene for 15 min by ultrasonic agitation (Misonix Ultrasonic Processor-XL) with a frequency of 20Hz in a water bath (10-15°C). After 15min the extract was taken out and then added freshly another 50ml of Toluene and then kept for agitation for another 15 min. These two extracts were mixed and were centrifuged at 4000 RPM for 20 min. The samples were filtered and then concentrated with the help of rotary evaporator to 0.5-2 ml.

PAHs in the samples were fractionated by a silica gel column (4mm i.d.). Three grams of silica gel (Silica gel 60, particle size 0.0630 – 0.200 mm, 70-230 mesh ASTM procured from Merck KgaA, Darmstadt, Germany) was activated at 180°C for 24 hours, and deactivated with 1% water. Then 40 ml of n-hexane was added to make a slurry, and was kept overnight for degassing. After degassing the slurry was packed in a column. Precaution was taken to avoid cracking of column. Hexane was eluted and the previously concentrated extract was transferred to the column. Column was eluted first with 10 ml of hexane and the elutant was discarded. Further elution was done by 20 ml of 1:1 hexane: toluene to obtain PAHs fractions (Caricchia et al., 1999). The fraction containing PAHs were concentrated to 0.5-2ml by rotary evaporator. The sample was filtered by 0.20 $\mu\text{m}$  nylon filter and then transferred in a clean vial and stored at 4°C till further analysis.

### **3.4 HPLC analysis: Qualification and Quantification**

The Waters HPLC system consisted of:

- Waters 510 HPLC Pump
- Waters 484 Tunable absorbance detector
- Waters Automated gradient controller
- Waters 746 data module
- Injection valve (20 $\mu\text{L}$ ),

The PAH residue were separated by HPLC, and the individual PAHs were quantified using reference PAH standard (Supelco Inc. USA), and pre-deuterated PAH standards using Waters PAH C<sub>18</sub> column. Gradient elution was executed with acetonitrile-water mixture. The PAH detection was made on a UV detector at wavelength 254 nm.

### 3.4.1 Operating Condition

Column	:	Waters PAH C <sub>18</sub> (4.6 x 250 mm, 5µm-particle size)
Temperature	:	28°C ± 0.3°C
Mobile phase	:	5 min 50%/50% acetonitrile/water 20 min 100% acetonitrile 28 min 100% acetonitrile 32 min 50%/50% acetonitrile/water
Flow rate	:	1.5 ml/min
Detector	:	UV-254 nm
Injection volume	:	20 µl

The column was equilibrated for 30min before the first analysis. All the analysis were made in triplicates.

### 3.4.2 Internal standard calibration

Sixteen PAHs (16 compounds specified in EPA Method 610) in a mixture and an internal standard consisting of Naphthalene-d<sub>8</sub>; Acenaphthene-d<sub>10</sub>; Phenanthrene-d<sub>10</sub>; Chrysene-d<sub>12</sub> and Perylene-d<sub>12</sub>, standards were obtained from Supelco (USA).

Calibration standards of three concentration levels of 0.5 ppm, 1ppm and 2.0 ppm of external standard were prepared by adding known constant amount of internal standards by diluting to 1000µl of volume with acetonitrile. The ratio of Internal to external standard was taken as 1:10.

Peak area responses was used against concentration for each compound and internal standard to calculate Response factor.

Response factors (RF) for each compound was used by (USEPA, 1996)

$$RF = \frac{(A_s) (C_{is})}{(A_{is}) (C_s)}$$

where,

A<sub>s</sub> = Response for the analyte to be measured

- $A_{is}$  = Response for the internal standard
- $C_{is}$  = Concentration of the internal standard (  $\mu\text{g/L}$  )
- $C_s$  = Concentration of the analyte to be measured (  $\mu\text{g/L}$  )

The working calibration curve, calibration factor, or RF were verified on each working day by preparing at least one calibration standard and assured that the variation was not more than  $\pm 15\%$ . If the variation was more than 15% the test was repeated using a fresh calibration standard.

Concentration in the sample using the response factor was calculated,

$$C (\mu\text{g/L}) = \frac{(A_s) (I_s)}{(A_{is}) (RF) (W)}$$

where,

- $A_s$  = Response for the parameter to be measured. s
- $A_{is}$  = Response for the internal standard. is
- $I_s$  = Amount of internal standard added to each extract (  $\mu\text{g}$  ).
- RF = Response Factor
- W = Volume of water extracted (L).

The calibration of the instrument was checked after each analytical run by analyzing 3 standard concentrations and a control standard.

### 3.5 QA/QC measures and performance

Before analysis, calibration standards were run to check column performance, peak height and resolution. With each batch of samples to be analyzed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times.

All data were subject to strict quality control procedures. Deuterated internal standards ( IS ) were used to compensate for losses involved in the sample extraction and work-up. The two IS themselves monitored were d12-Chry and d10-Phen.

The response factor (RF) of the standard PAHs relative to the internal standard was determined by analyzing the standard 16 PAH compounds containing the internal standard (IS) on the HPLC. The response factors were obtained using the equation.

## *Chapter IV*

### *Results and Discussion*

## RESULTS AND DISCUSSION

In the present study five sites were selected by taking one site (Ram Ghat) upstream to the city, three sites in the middle segment (NGUS, NGDS and ITO) and one site lower stream to the city (Okhla). Sediment samples were collected from these sites. In the sediment samples, different PAHs viz. 3-ring, *Phen* and *Anth*, 4-ring, *Fl*, *Pyr*, *B[a]A* and *Chry*, 5-ring *B[b]F*, *B[k]F*, *B[a]P* and *DB[a,h]A* and 6-ring *B[g,h,i]P* and *IP* were analyzed and the results are tabulated in Table 4.1-4.5. Seasonal variation in Pre-monsoon (June), monsoon (August) and Post-monsoon (September) period was also taken into consideration. Seasonal variation of *B[a]P* has been discussed separately. Percentage distribution of individual PAHs has been worked out. PAH isomer pair ratios were used for the source identification.

### 4.1 Spatial and temporal variation of total concentrations of the 12 PAHs and relative distribution of individual PAHs

In this study five sampling stations were chosen and the individual PAHs at different sites is depicted in Fig 4.1. Total concentration of the 12 PAHs studied in the sediments is expressed as  $\sum_{12} \text{PAH}$ . It spanned from 4.82-47.83 ng/g with a mean of  $15.00 \pm 7.86$  ng/g. The highest average seasonal concentration was found at ITO ( $20.94 \pm 13.60$  ng/g), while minimum concentration was at RG ( $10.59 \pm 2.89$  ng/g). At other sites viz. NGUS, NGDS and OK the concentrations of  $\sum_{12} \text{PAH}$  were  $11.90 \pm 6.08$ ,  $16.53 \pm 3.69$  and  $15.04 \pm 6.84$  ng/g respectively.

At all the sites  $\sum_{12} \text{PAH}$  concentrations shows an increasing trend from pre- to post-monsoon being minimum during monsoon.

At all the sites investigated in the present study, tetra-cyclic PAH (*B[a]A*, *Chry*, *Fl* and *Pyr*) concentrations dominated. Other abundant compounds were *Anth* (a three ring compound) and *B[k]F* (a five ring compound).

Average *Anth* concentration ranged from 0.98 ng/g (Okhla) to 1.60 ng/g (ITO). Among four ring compounds *Fl* reached maximum average concentration of 3.26 ng/g at ITO and minimum at NGUS (1.82 ng/g). *Pyr* concentration was also found maximum at ITO (4.93 ng/g) and minimum at Okhla (1.66 ng/g). *B[a]A* was the most abundant compound at ITO, NGUS

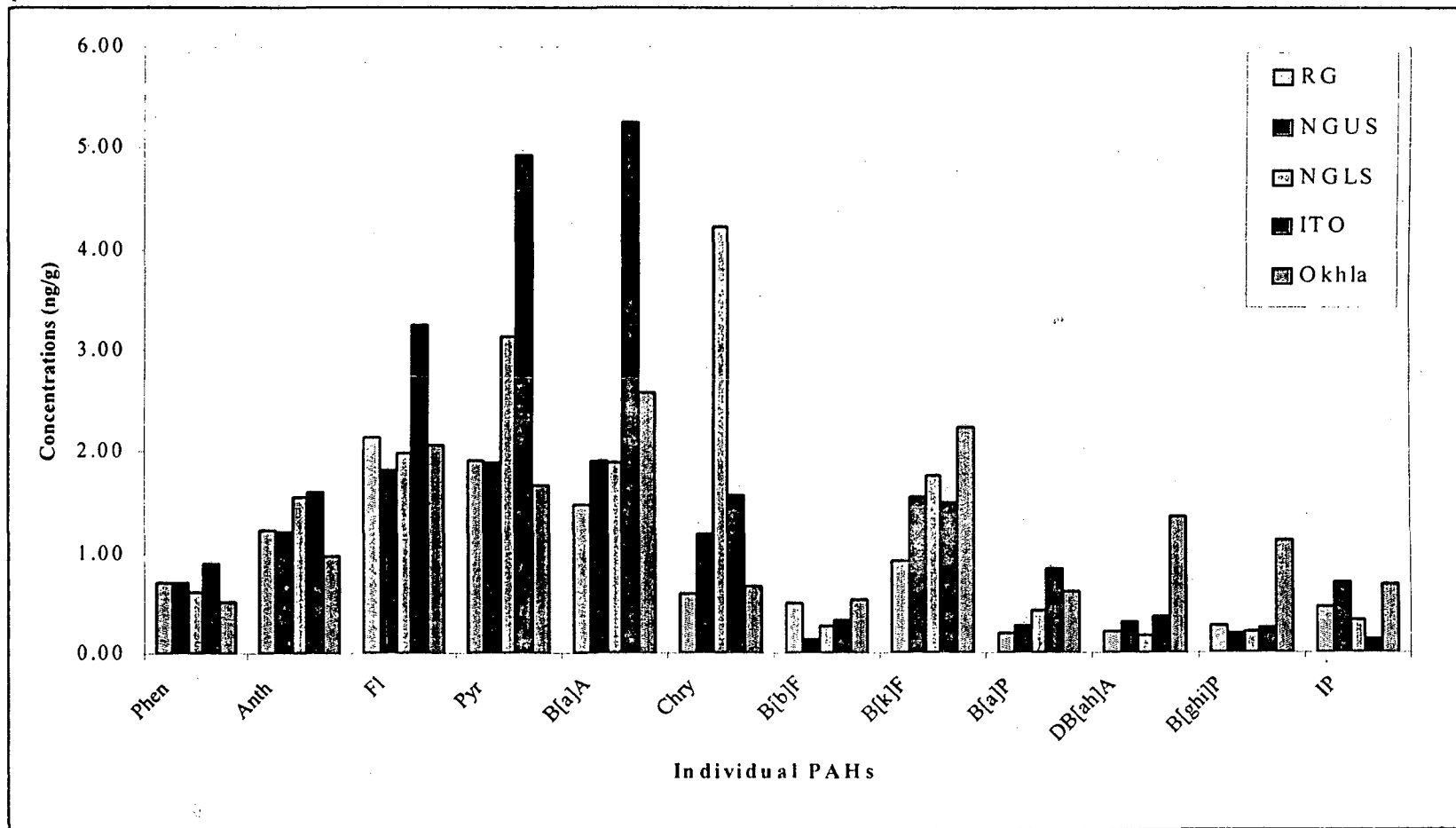


Fig. 4.1: Concentrations (ng/g) of Individual PAHs at different sites in Sediment (<53μm) of River Yamuna



and Okhla. Maximum average concentration was at ITO (5.25 ng/g) and minimum at RG (1.47 ng/g). While for *Chry* maximum concentration was at NGDS (4.21 ng/g) and minimum at RG (0.59 ng/g).

Among five ring compounds *B[k]F* was the only compound that was relatively abundant. Average concentration of *B[k]F* reached a maximum value of 2.23 ng/g at Okhla and minimum value of 0.93 ng/g at RG.

#### 4.1 a) Ramghat (RG)

At Ramghat  $\sum_{12}$ PAH concentration ranged from 8.45-14.44 ng/g with a mean of  $10.59 \pm 2.89$  ng/g (Table 4.1) between June and September 2003. Maximum  $\sum_{12}$ PAH was during post-monsoon season (September) with a mean of  $13.88 \pm 0.49$  ng/g. Mean of  $\sum_{12}$ PAH concentrations during pre-monsoon (June) and monsoon (August) concentrations were  $9.40 \pm 0.15$  ng/g and  $8.49 \pm 0.06$  ng/g respectively.

During pre-monsoon (Fig. 4.2) *Anth* was observed to be highest which ranged from 1.77-1.82 ng/g with a mean of  $1.80 \pm 0.03$  ng/g. Other four ring compounds were also found to be in significant amounts while among five-ring compounds *B[a]P* was present in considerable amounts.

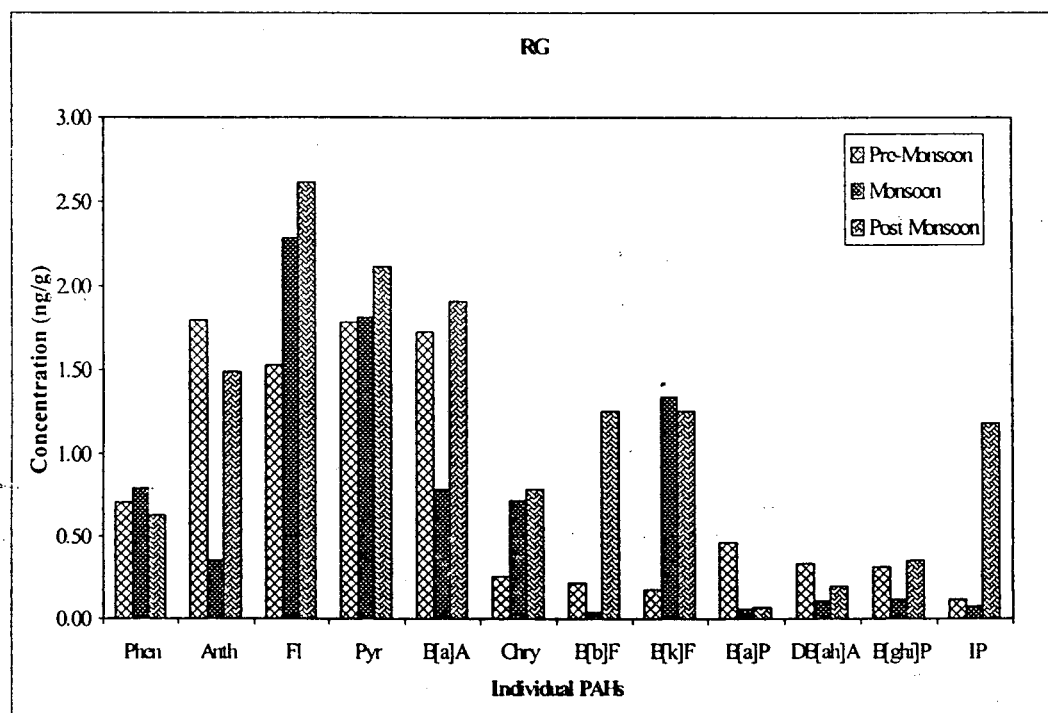


Fig 4.2: Seasonal variation (ng/g) of Individual PAHs at Ram Ghat

**Table 4.1:** Concentrations of PAHs (ng/g) during Pre-Monsoon, Monsoon and Post-Monsoon in surficial sediments (<53 $\mu$ m) of river Yamuna at RG

Season	Phen	Anth	Fl	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[a]P	Db[ah]A	B[ghi]P	IP	$\Sigma_{12}$ PAHs
Pre-Monsoon	0.71	1.77	1.50	1.76	1.72	0.26	0.21	0.18	0.47	0.34	0.34	0.12	9.37
	0.68	1.80	1.52	1.79	1.75	0.29	0.25	0.20	0.50	0.35	0.32	0.10	9.56
	0.72	1.82	1.55	1.80	1.70	0.22	0.18	0.15	0.40	0.30	0.29	0.12	9.28
<b>Average</b>	<b>0.70</b>	<b>1.80</b>	<b>1.53</b>	<b>1.78</b>	<b>1.72</b>	<b>0.26</b>	<b>0.21</b>	<b>0.18</b>	<b>0.46</b>	<b>0.33</b>	<b>0.32</b>	<b>0.11</b>	<b>9.40</b>
SD	0.02	0.03	0.03	0.02	0.02	0.03	0.04	0.03	0.05	0.03	0.02	0.01	0.15
Monsoon	0.76	0.36	2.20	1.81	0.85	0.68	0.04	1.40	0.06	0.11	0.12	0.07	8.46
	0.80	0.31	2.34	1.74	0.80	0.75	0.02	1.35	0.05	0.09	0.12	0.05	8.45
	0.82	0.40	2.31	1.90	0.70	0.70	0.05	1.28	0.06	0.11	0.10	0.10	8.55
<b>Average</b>	<b>0.79</b>	<b>0.36</b>	<b>2.28</b>	<b>1.82</b>	<b>0.78</b>	<b>0.71</b>	<b>0.04</b>	<b>1.35</b>	<b>0.06</b>	<b>0.10</b>	<b>0.12</b>	<b>0.07</b>	<b>8.49</b>
SD	0.03	0.05	0.07	0.08	0.08	0.04	0.01	0.06	0.01	0.01	0.01	0.02	0.06
Post-Monsoon	0.62	1.29	2.61	2.09	1.89	0.78	1.18	1.26	0.10	0.23	0.36	1.10	13.52
	0.52	1.50	2.50	2.15	1.90	0.76	1.28	1.30	0.06	0.20	0.29	1.20	13.69
	0.75	1.69	2.76	2.10	1.96	0.82	1.30	1.19	0.05	0.15	0.40	1.25	14.44
<b>Average</b>	<b>0.63</b>	<b>1.49</b>	<b>2.62</b>	<b>2.12</b>	<b>1.92</b>	<b>0.79</b>	<b>1.26</b>	<b>1.25</b>	<b>0.07</b>	<b>0.19</b>	<b>0.35</b>	<b>1.19</b>	<b>13.88</b>
SD	0.12	0.20	0.13	0.03	0.04	0.03	0.06	0.06	0.02	0.04	0.06	0.08	0.49
<b>Toatal average</b>	<b>0.71</b>	<b>1.22</b>	<b>2.14</b>	<b>1.91</b>	<b>1.47</b>	<b>0.59</b>	<b>0.50</b>	<b>0.93</b>	<b>0.20</b>	<b>0.21</b>	<b>0.26</b>	<b>0.46</b>	<b>10.59</b>

During monsoon *Anth* decreased to a value which ranged from 0.31-0.40 ng/g with a mean of  $0.36 \pm 0.05$  ng/g. *Fl* was observed to be maximum with a range 2.20-2.34 ng/g and the mean was  $2.28 \pm 0.07$  ng/g while *Pyr* was also considerably high. Among the five ring compounds *B[k]F* was present in considerable amount. Concentrations of *B[k]F* ranged from 1.28-1.40 ng/g with a mean of  $1.35 \pm 0.06$  ng/g.

Though the concentration of *Fl* was high throughout all the three seasons it followed an increasing trend. During post-monsoon *Fl* concentration ranged from 2.50-2.76 ng/g with a mean of  $2.62 \pm 0.13$  ng/g. During post-monsoon *B[b]F*, *B[k]F* and *IP* were also present in considerable amounts.

#### 4.1 b) Najafgarh Upstream (NGUS)

At Najafgarh upstream total  $\sum_{12}$ PAH concentration ranged from 4.82-16.64 ng/g with a mean of  $11.90 \pm 6.08$  ng/g (Table 4.2). Maximum  $\sum_{12}$ PAH was maximum during post-monsoon season with a mean of  $16.46 \pm 0.20$  ng/g.  $\sum_{12}$ PAH concentrations during pre-monsoon were in the range 13.92-14.54 ng/g with a mean of  $14.24 \pm 0.31$  ng/g and during monsoon concentrations ranged from 4.82-5.13 ng/g with a mean of  $4.99 \pm 0.16$  ng/g respectively.

During pre-monsoon *Fl* was present (Fig 4.3) in highest amount with a mean value of  $3.13 \pm 0.13$  ng/g. Among the five ring compounds *B[k]F* and *IP* were observed in significant amount with a mean concentration of  $1.57 \pm 0.06$  ng/g and  $1.88 \pm 0.08$  ng/g respectively.

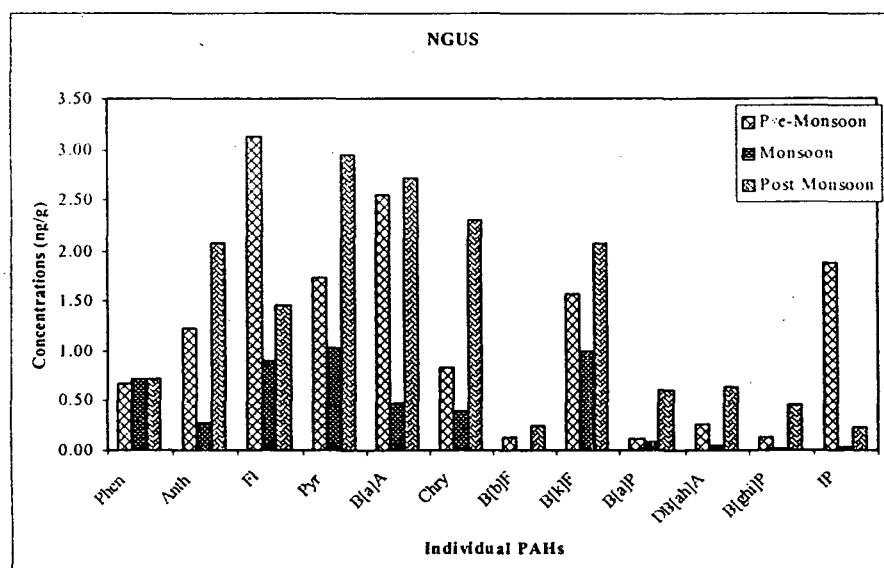


Fig 4.3: Seasonal variation (ng/g) of Individual PAHs at Najafgarh Upstream

**Table 4.2:** Concentrations of PAHs (ng/g) during Pre-Monsoon, Monsoon and Post-Monsoon in surficial sediments (<53 $\mu$ m) of river Yamuna at NGUS

Season	Phen	Anth	Fl	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[a]P	Db[ah]A	B[ghi]P	IP	$\Sigma_{12}$ PAHs
Pre-Monsoon (June)	0.60	1.27	3.13	1.87	2.46	0.79	0.13	1.58	0.14	0.24	0.13	1.97	14.28
	0.68	1.15	3.00	1.70	2.50	0.85	0.10	1.63	0.12	0.25	0.10	1.80	13.92
	0.71	1.28	3.25	1.62	2.71	0.87	0.16	1.51	0.10	0.30	0.15	1.86	14.54
<b>Average</b>	<b>0.66</b>	<b>1.23</b>	<b>3.13</b>	<b>1.73</b>	<b>2.56</b>	<b>0.84</b>	<b>0.13</b>	<b>1.57</b>	<b>0.12</b>	<b>0.27</b>	<b>0.13</b>	<b>1.88</b>	<b>14.24</b>
SD	0.06	0.07	0.13	0.12	0.14	0.04	0.03	0.06	0.02	0.03	0.02	0.08	0.31
Monsoon (July)	0.69	0.28	0.90	1.02	0.47	0.40	0.00	1.03	0.10	0.06	0.06	0.03	5.02
	0.72	0.26	0.83	1.00	0.45	0.38	0.00	1.00	0.08	0.06	0.00	0.02	4.82
	0.75	0.32	0.95	1.06	0.50	0.42	0.00	0.98	0.07	0.03	0.00	0.05	5.13
<b>Average</b>	<b>0.72</b>	<b>0.29</b>	<b>0.89</b>	<b>1.03</b>	<b>0.47</b>	<b>0.40</b>	<b>0.00</b>	<b>1.00</b>	<b>0.08</b>	<b>0.05</b>	<b>0.02</b>	<b>0.03</b>	<b>4.99</b>
SD	0.03	0.03	0.06	0.03	0.03	0.02	0.00	0.02	0.01	0.02	0.03	0.02	0.16
Post-Monsoon (September)	0.72	2.14	1.45	2.99	2.70	2.32	0.28	2.09	0.61	0.64	0.46	0.25	16.64
	0.72	2.00	1.50	3.00	2.80	2.20	0.25	2.10	0.65	0.60	0.45	0.20	16.49
	0.70	2.10	1.40	2.84	2.65	2.41	0.22	2.06	0.54	0.65	0.44	0.22	16.25
<b>Average</b>	<b>0.71</b>	<b>2.08</b>	<b>1.45</b>	<b>2.94</b>	<b>2.72</b>	<b>2.31</b>	<b>0.25</b>	<b>2.08</b>	<b>0.60</b>	<b>0.63</b>	<b>0.45</b>	<b>0.23</b>	<b>16.46</b>
SD	0.01	0.07	0.05	0.09	0.08	0.10	0.03	0.02	0.05	0.03	0.01	0.03	0.20
<b>Toatal average</b>	<b>0.70</b>	<b>1.20</b>	<b>1.82</b>	<b>1.90</b>	<b>1.92</b>	<b>1.18</b>	<b>0.13</b>	<b>1.55</b>	<b>0.27</b>	<b>0.31</b>	<b>0.20</b>	<b>0.71</b>	<b>11.90</b>

During monsoon *Pyr* was found to be maximum, for which concentration ranged from 1.00-1.06 ng/g with a mean of  $1.03 \pm 0.03$  ng/g. *B[k]F* was the second most abundant compound which ranged between 0.98-1.03 ng/g with a mean of  $1.00 \pm 0.02$  ng/g. Among other four ring compounds concentrations for *Fl*, *B[a]A* and *Chry* were found to be very less. Concentration of other five ring compounds was not significant.

During post-monsoon also, concentration of *Pyr* was found to be maximum and ranged between 2.84-3.00 ng/g with a mean of  $2.94 \pm 0.09$  ng/g. Second highest concentration was for *B[a]A* that ranged from 2.65-2.80 ng/g with a mean of  $2.72 \pm 0.08$  ng/g. Among five ring compounds *B[k]F* was found in significant amounts. For *B[k]F* concentrations ranged from 2.06-2.10 ng/g with a mean of  $2.08 \pm 0.02$  ng/g. Concentrations for other five ring compounds were not significant.

#### 4.1. c) Najafgarh Downstream (NGDS)

At NGDS total PAH concentration ranged from 13.42-21.33 ng/g with a mean of (Table 4.3)  $16.53 \pm 3.69$  ng/g. Maximum  $\sum_{12}$ PAH was during post-monsoon season with a mean of  $20.66 \pm 0.84$  ng/g. Mean of  $\sum_{12}$ PAH concentrations during pre-monsoon and monsoon concentrations were  $15.38 \pm 0.40$  ng/g and  $13.55 \pm 0.12$  ng/g respectively.

During pre-monsoon *Pyr* (Fig. 4.4) was present in highest amount and the concentrations

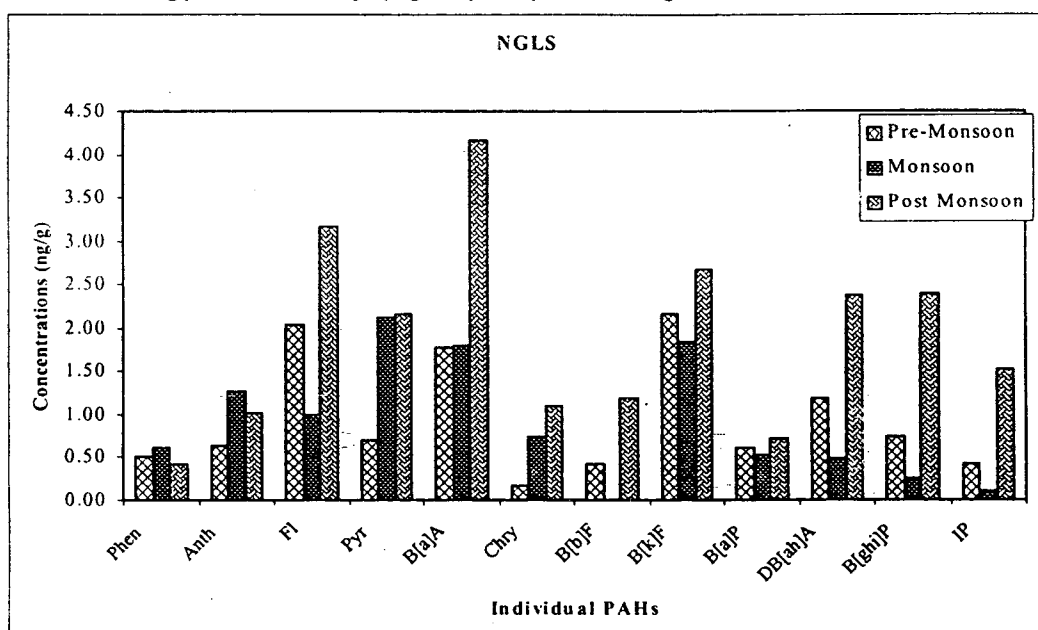


Fig 4.4: Seasonal variation (ng/g) of Individual PAHs at Najafgarh downstream

**Table 4.3:** Concentrations of PAHs (ng/g) during Pre-Monsoon, Monsoon and Post-Monsoon in surficial sediments (<53µm) of river Yamuna at NGLS

Season	Phen	Anth	Fl	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[a]P	Db[ah]A	B[ghi]P	IP	Σ <sub>12</sub> PAHs
Pre-Monsoon (June)	0.74	2.17	1.49	3.04	1.76	2.29	0.29	2.06	0.63	0.38	0.41	0.26	15.53
	0.70	2.00	1.45	3.00	1.74	2.20	0.25	2.00	0.60	0.35	0.40	0.22	14.93
	0.75	2.19	1.50	3.04	1.78	2.30	0.29	2.10	0.63	0.41	0.42	0.28	15.70
<b>Average</b>	<b>0.73</b>	<b>2.12</b>	<b>1.48</b>	<b>3.03</b>	<b>1.76</b>	<b>2.26</b>	<b>0.28</b>	<b>2.06</b>	<b>0.62</b>	<b>0.38</b>	<b>0.41</b>	<b>0.25</b>	<b>15.38</b>
SD	0.02	0.10	0.03	0.02	0.02	0.05	0.02	0.05	0.02	0.03	0.01	0.03	0.40
Monsoon (July)	0.76	0.91	2.75	2.97	1.97	1.85	0.42	1.59	0.05	0.01	0.08	0.05	13.42
	0.70	1.01	2.81	3.01	1.81	1.90	0.46	1.66	0.07	0.02	0.10	0.04	13.58
	0.62	0.96	2.90	2.76	2.03	2.00	0.51	1.70	0.01	0.01	0.08	0.07	13.65
<b>Average</b>	<b>0.70</b>	<b>0.96</b>	<b>2.82</b>	<b>2.91</b>	<b>1.93</b>	<b>1.92</b>	<b>0.46</b>	<b>1.65</b>	<b>0.04</b>	<b>0.01</b>	<b>0.08</b>	<b>0.05</b>	<b>13.55</b>
SD	0.07	0.05	0.08	0.13	0.11	0.08	0.04	0.05	0.03	0.01	0.01	0.01	0.12
Post-Monsoon (September)	0.48	1.78	1.70	3.20	1.87	8.88	0.07	1.66	0.59	0.15	0.16	0.79	21.33
	0.30	1.58	1.58	3.40	1.91	8.00	0.06	1.50	0.56	0.14	0.17	0.50	19.72
	0.51	1.29	1.71	3.80	2.10	8.50	0.05	1.48	0.55	0.13	0.14	0.65	20.93
<b>Average</b>	<b>0.43</b>	<b>1.55</b>	<b>1.66</b>	<b>3.47</b>	<b>1.96</b>	<b>8.46</b>	<b>0.06</b>	<b>1.55</b>	<b>0.57</b>	<b>0.14</b>	<b>0.16</b>	<b>0.65</b>	<b>20.66</b>
SD	0.12	0.25	0.07	0.30	0.13	0.44	0.01	0.10	0.02	0.01	0.02	0.14	0.84
<b>Total average</b>	<b>0.62</b>	<b>1.54</b>	<b>1.99</b>	<b>3.14</b>	<b>1.88</b>	<b>4.21</b>	<b>0.27</b>	<b>1.75</b>	<b>0.41</b>	<b>0.18</b>	<b>0.22</b>	<b>0.32</b>	<b>16.53</b>

ranged from 3.00-3.04 ng/g with a mean of  $3.03 \pm 0.02$  ng/g. Among five ring compounds *B[k]F* was present in significant amounts for which concentration ranged from 2.00-2.10 ng/g with a mean of  $2.06 \pm 0.05$  ng/g.

During monsoon also *Pyr* was found to be maximum, and concentration ranged from 2.76-3.01 ng/g with a mean of  $2.91 \pm 0.13$  ng/g. *Fl* was the second most abundant compound which ranged between 2.75-2.90 ng/g with a mean of  $2.82 \pm 0.08$  ng/g. Among the five ring compounds *B[k]F* was present in considerable amount. Concentrations of *B[k]F* was also found to be reduced to a mean value of  $1.65 \pm 0.05$  ng/g.

During post-monsoon, concentration of *Chry* was found to be very high which ranged from 8.00-8.88 ng/g with a mean of  $8.46 \pm 0.44$  ng/g.

#### 4.1 d) Income Tax Office (ITO)

At ITO total PAH concentration ranged from 10.81-47.83 ng/g with a mean of  $20.94 \pm 13.60$  ng/g (Table 4.4). Maximum  $\sum_{12}$ PAH was observed during post-monsoon season with a mean concentration of  $38.08 \pm 8.55$  ng/g.  $\sum_{12}$ PAH concentrations during pre-monsoon were in the range of 13.68-14.04 ng/g with a mean of  $13.82 \pm 0.19$  ng/g and during monsoon the concentrations ranged from 10.81-11.01 ng/g with a mean of  $10.93 \pm 0.10$  ng/g.

Among five ring compounds *B[k]F* concentration was observed higher again indicating towards motor vehicular source.

During pre-monsoon *Fl* (Fig. 4.5) concentration was highest with a mean of  $3.45 \pm 0.35$  ng/g.

During monsoon also *Fl* was found to be maximum, for which concentration ranged from 1.90-2.08 ng/g with a mean of  $1.98 \pm 0.09$  ng/g. *Anth* was the second most abundant compound which ranged between 1.80-1.91 ng/g with a mean of  $1.85 \pm 0.05$  ng/g.

During post-monsoon, concentration of *B[a]A* was found to be very high, in the range of 7.51-16.51 ng/g with a mean of  $11.43 \pm 4.61$  ng/g. Second highest concentration was for *Pyr*, which ranged between 8.00-15.12 ng/g with a mean of  $10.89 \pm 3.74$  ng/g. Among the five ring compounds *B[k]F*, *B[a]P* and *DB[ah]A* were found in significant amounts. For *B[a]P* concentrations ranged from 1.43-1.60 ng/g with a mean of  $1.51 \pm 0.09$  ng/g. The concentration

**Table 4.4:** Concentrations of PAHs (ng/g) during Pre-Monsoon, Monsoon and Post-Monsoon in surficial sediments (<53 $\mu$ m) of river Yamuna at ITO

Season	Phen	Anth	Fl	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[a]P	Db[ah]A	B[ghi]P	IP	$\Sigma_{12}$ PAHs
Pre-Monsoon (June)	0.69	1.18	3.46	2.30	2.95	1.48	0.20	0.74	0.55	0.04	0.07	0.02	13.68
	0.73	1.20	3.10	2.51	3.20	1.51	0.15	0.80	0.60	0.03	0.09	0.10	14.04
	0.66	1.16	3.80	2.01	2.80	1.47	0.20	0.80	0.65	0.07	0.09	0.04	13.75
<b>Average</b>	<b>0.69</b>	<b>1.18</b>	<b>3.45</b>	<b>2.28</b>	<b>2.99</b>	<b>1.48</b>	<b>0.18</b>	<b>0.78</b>	<b>0.60</b>	<b>0.04</b>	<b>0.08</b>	<b>0.06</b>	<b>13.82</b>
SD	0.03	0.02	0.35	0.25	0.20	0.02	0.03	0.03	0.05	0.02	0.01	0.04	0.19
Monsoon (July)	0.80	1.80	1.90	1.50	1.41	1.10	0.20	1.60	0.41	0.03	0.04	0.00	10.81
	0.80	1.80	1.90	1.50	1.41	1.10	0.20	1.60	0.41	0.03	0.04	0.00	10.81
	0.78	1.91	2.08	1.72	1.30	1.00	0.18	1.51	0.43	0.00	0.02	0.01	10.96
<b>Average</b>	<b>0.79</b>	<b>1.85</b>	<b>1.98</b>	<b>1.63</b>	<b>1.35</b>	<b>1.06</b>	<b>0.19</b>	<b>1.57</b>	<b>0.42</b>	<b>0.02</b>	<b>0.04</b>	<b>0.01</b>	<b>10.93</b>
SD	0.01	0.05	0.09	0.11	0.06	0.05	0.01	0.05	0.01	0.02	0.01	0.01	0.10
Post-Monsoon (September)	1.25	1.80	4.40	15.12	16.51	2.44	0.62	2.25	1.43	1.04	0.62	0.35	47.83
	1.20	1.70	4.20	9.54	7.51	1.58	0.65	2.00	1.50	1.00	0.62	0.30	31.83
	1.18	1.80	4.41	8.00	10.25	2.50	0.59	2.15	1.60	1.10	0.65	0.32	34.57
<b>Average</b>	<b>1.21</b>	<b>1.77</b>	<b>4.34</b>	<b>10.89</b>	<b>11.43</b>	<b>2.18</b>	<b>0.62</b>	<b>2.14</b>	<b>1.51</b>	<b>1.05</b>	<b>0.63</b>	<b>0.33</b>	<b>38.08</b>
SD	0.03	0.06	0.12	3.74	4.61	0.51	0.03	0.13	0.09	0.05	0.02	0.03	8.55
<b>Toatal average</b>	<b>0.74</b>	<b>1.52</b>	<b>2.72</b>	<b>1.95</b>	<b>2.17</b>	<b>1.27</b>	<b>0.19</b>	<b>1.18</b>	<b>0.51</b>	<b>0.03</b>	<b>0.06</b>	<b>0.03</b>	<b>12.37</b>



of *B[a]P* was observed in significant concentration at this site only during post-monsoon season.

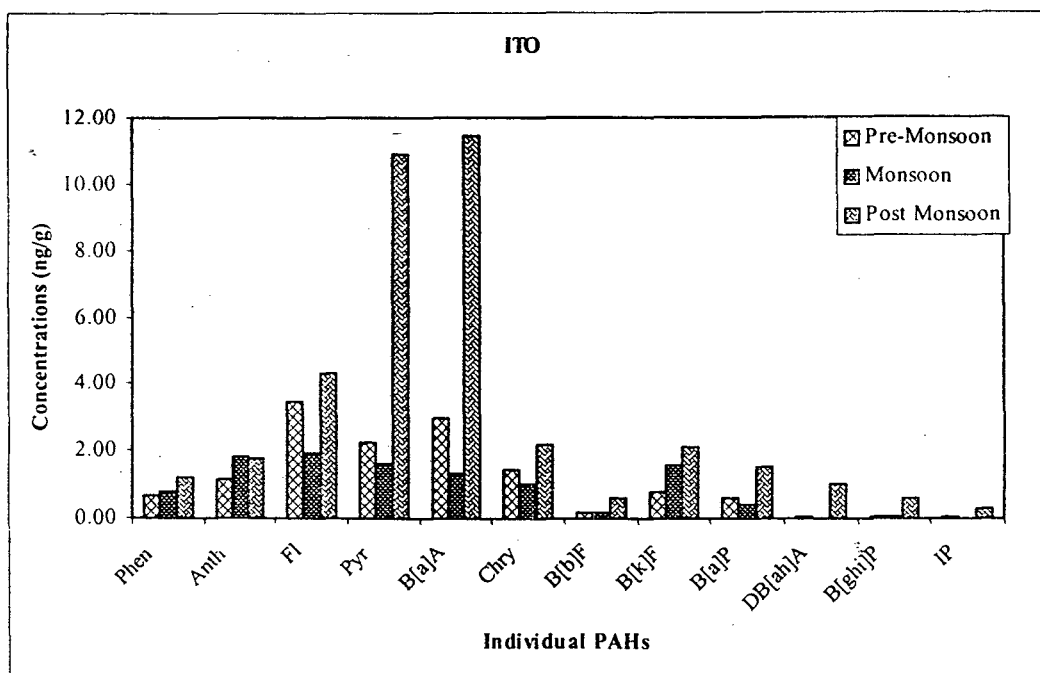


Fig 4.5: Seasonal variation (ng/g) of Individual PAHs at ITO

#### 4.1 e) Okhla (OK)

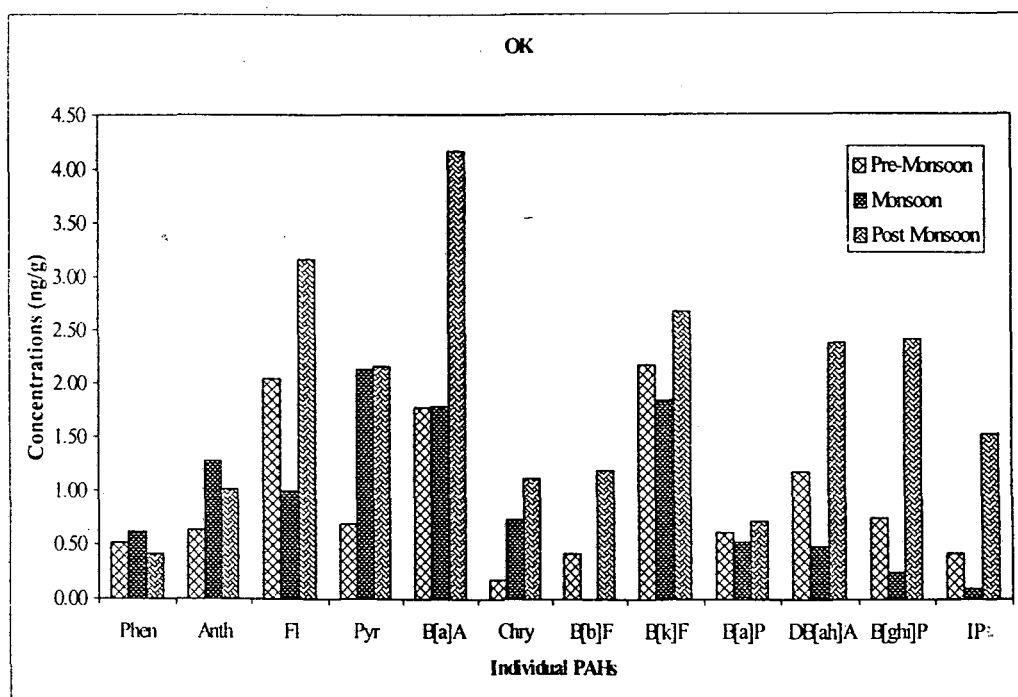
At Okhla total PAH concentration ranged from 10.67-23.07 ng/g with a mean of  $15.04 \pm 6.84$  ng/g (Table 4.5). Maximum  $\sum_{12}$ PAH was observed during post-monsoon season with a mean of  $22.93 \pm 0.16$  ng/g.  $\sum_{12}$ PAH concentrations during pre-monsoon were in the range 11.13-11.66 ng/g with a mean of  $11.41 \pm 0.27$  ng/g and during monsoon concentrations ranged from 10.67-10.97 ng/g with a mean of  $10.78 \pm 0.16$  ng/g.

During pre-monsoon concentration of *B[k]F* (Fig. 4.6) was highest with a mean of  $2.17 \pm 0.02$  ng/g. Among the four ring compounds the concentrations for *Fl* was maximum which spanned from 2.01-2.06 ng/g with a mean of  $2.04 \pm 0.02$  ng/g. Among the five ring compounds *B[k]F* and *DB[ah]A* were observed to be in significant amount.

During monsoon *Pyr* was observed to be maximum, for which the concentration ranged from 2.00-2.20 ng/g with a mean of  $2.13 \pm 0.11$  ng/g. *B[k]F* was the second most abundant compound which ranged between 1.71-1.94 ng/g with a mean of  $1.85 \pm 0.12$  ng/g. *B[k]F* was present in considerable amount for which concentration ranged from 1.71-1.94 ng/g with a mean of  $1.85 \pm 0.12$  ng/g.

**Table 4.5:** Concentrations of PAHs (ng/g) during Pre-Monsoon, Monsoon and Post-Monsoon in surficial sediments (<53 $\mu$ m) of river Yamuna at OK

Season	Phen	Anth	Fl	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[a]P	Db[ah]A	B[ghi]P	IP	$\Sigma_{12}$ PAHs
Pre-Monsoon (June)	0.51	0.64	2.04	0.69	1.78	0.18	0.43	2.17	0.61	1.18	0.76	0.44	11.45
	0.50	0.62	2.01	0.65	1.75	0.15	0.40	2.15	0.60	1.17	0.70	0.40	11.13
	0.52	0.64	2.06	0.74	1.80	0.20	0.45	2.19	0.62	1.19	0.78	0.45	11.66
<b>Average</b>	<b>0.51</b>	<b>0.63</b>	<b>2.04</b>	<b>0.70</b>	<b>1.78</b>	<b>0.18</b>	<b>0.43</b>	<b>2.17</b>	<b>0.61</b>	<b>1.18</b>	<b>0.75</b>	<b>0.43</b>	<b>11.41</b>
SD	0.01	0.01	0.02	0.04	0.03	0.03	0.03	0.02	0.01	0.01	0.04	0.03	0.27
Monsoon (July)	0.62	1.29	0.99	2.18	1.80	0.74	0.01	1.89	0.52	0.49	0.29	0.15	10.97
	0.58	1.25	1.00	2.20	1.81	0.72	0.00	1.71	0.50	0.49	0.25	0.16	10.67
	0.65	1.30	1.00	2.00	1.79	0.76	0.00	1.94	0.55	0.50	0.20	0.00	10.69
<b>Average</b>	<b>0.62</b>	<b>1.28</b>	<b>0.99</b>	<b>2.13</b>	<b>1.80</b>	<b>0.74</b>	<b>0.00</b>	<b>1.85</b>	<b>0.53</b>	<b>0.49</b>	<b>0.25</b>	<b>0.10</b>	<b>10.78</b>
SD	0.03	0.02	0.01	0.11	0.01	0.02	0.01	0.12	0.03	0.01	0.04	0.09	0.16
Post-Monsoon (September)	0.48	0.96	3.25	2.06	4.16	1.11	1.16	2.60	0.77	2.53	2.56	1.41	23.07
	0.40	1.01	3.19	2.20	4.19	1.10	1.20	2.70	0.70	2.20	2.25	1.58	22.76
	0.36	1.09	3.04	2.22	4.12	1.12	1.21	2.71	0.69	2.40	2.40	1.60	22.98
<b>Average</b>	<b>0.42</b>	<b>1.02</b>	<b>3.16</b>	<b>2.16</b>	<b>4.16</b>	<b>1.11</b>	<b>1.19</b>	<b>2.67</b>	<b>0.72</b>	<b>2.38</b>	<b>2.41</b>	<b>1.53</b>	<b>22.93</b>
SD	0.06	0.06	0.11	0.09	0.04	0.01	0.03	0.06	0.04	0.17	0.16	0.10	0.16
<b>Toatal average</b>	<b>0.51582</b>	<b>0.97828</b>	<b>2.06492</b>	<b>1.66273</b>	<b>2.57814</b>	<b>0.67611</b>	<b>0.54187</b>	<b>2.22884</b>	<b>0.62027</b>	<b>1.35152</b>	<b>1.13397</b>	<b>0.68871</b>	<b>15.041175</b>



**Fig 4.6:** Seasonal variation (ng/g) of Individual PAHs at Okhla

During post-monsoon, concentration of *B[a]A* was found to be considerably high, in the range 4.12-4.19 ng/g with a mean of  $4.16 \pm 0.04$  ng/g. Second highest concentration was *Fl* which ranged from 3.04-3.25 ng/g with a mean of  $3.16 \pm 0.11$  ng/g. Concentration of *Pyr* varied from 2.06-2.22 ng/g with a mean of  $2.16 \pm 0.09$  ng/g. Among other five ring compounds *B[b]F*, *DB[ah]A*, *B[ghi]P* and *IP* were found in significant amounts.

#### 4.2 Discussion

The analysis of PAHs in surficial sediment of the River Yamuna showed that  $\sum_{12}$  PAH concentrations were heterogeneously distributed at different sites throughout the river. Differences were observed among various segments of the river. The processes controlling the level of PAHs in the sediment are complex. Among important factors are chemical properties of the compounds (especially their water solubility), the composition of sediment such as organic carbon and clay content (Yang et al., 1998), and sedimentary depositional patterns so, many chemical, biological, and physical factors such as the combustion temperature of organic material during PAH formation, photo-oxidation, transport mechanisms, weathering, dilution effect, solubility, biodegradation, sampling scheme, and natural formation could have influenced the concentration of PAHs found throughout the river. Nevertheless, the concentration measured

in this snapshot represent a steady-state equilibrium at that point in time that resulted from the interactions of all of these factors. No attempts were made to measure these variables, although the concentration of PAHs measured should be generally indicative of nearby or adjoining land use. Accordingly, in this evaluation, differences in PAH concentration were observed at different stations.

Variation in the concentration of  $\sum_{12}$ PAH in the river Yamuna sediment are depicted in Fig. 4.7. It shows that significantly higher  $\sum_{12}$ PAH concentrations were found in the middle segment of the river being maximum at ITO and at downstream from the point where Najafgarh drain (largest drain entering into Yamuna) joins Yamuna as compared to stations upstream or downstream from the city. However at downstream from the city i.e. at Okhla,  $\sum_{12}$ PAH concentrations was lower than the concentration at ITO but comparable to that of NGDS. This finding is consistent with studies from other geographical locations (e.g., Australia, Maher and Aislabie 1992; Mediterranean Sea, Baumard *et al.* 1998; western Baltic Sea, Baumard *et al.* 1999; San Francisco Bay, Pereria *et al.* 1999; Kyeonggi Bay, Korea, Kim Gi *et al.* 1999; Baltimore Harbor, Ashley and Baker 1999), which support the conclusion that urbanized and industrialized areas are major sources of PAH contamination into sediments.

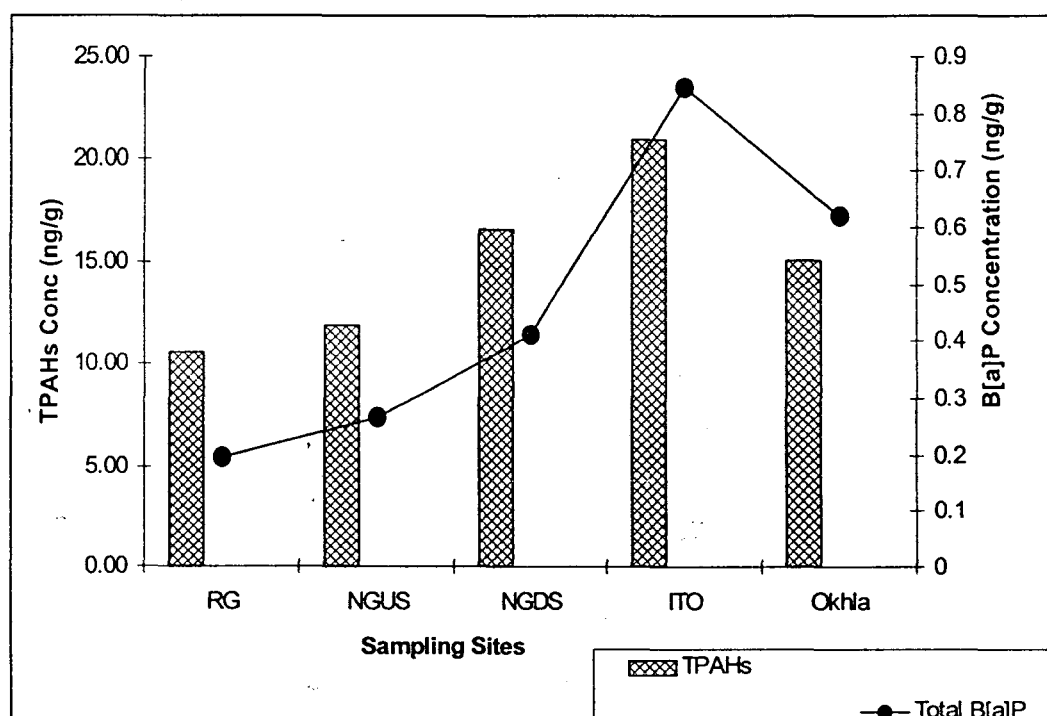


Fig 4.7: Variation of B[a]P and TPAHs at different sites

The  $\sum_{12}$ PAH concentration in river Yamuna sediments were lower as compared to the concentrations reported upon in rivers in other countries. Total PAH concentration reported in the literature frequently include different compounds (i.e. not the 12 US EPA priority pollutants studied here), and it has been suggested that *Fl* levels may provide a less ambiguous measure of comparing data from different areas (Heit, 1985), while *B[a]P* being highly carcinogenic, a comparison of *Fl* and *B[a]P* concentrations from different locations around the world shows that in river Yamuna sediment PAHs concentration (*Fl* was 0.89-4.34 ng/g and *B[a]P* 0.04-1.51 ng/g) are comparatively lower than that reported for sediments from river Ganges, India (*Fl* (value not given), 8 ng/g of *B[a]P*), Tonghui River, Beijing (16.25-62.4 ng/g of *Fl* and 11.01-6.26ng/g of *B[a]P*), Gao-Ping river, Taiwan (< 3-15.4 ng/g of *Fl* and <8-20 ng/g of *B[a]P*), Porto Torres Harbor (10-30 ng/g of *Fl* and 10-190 ng/g of *B[a]P*), Todos Santos bay, Baja California, Mexico (1.4-120.6 ng/g of *Fl* and 0.7-79 ng/g of *BaP*), the South China Sea (1.6-55.7 ng/g of *Fl* and 0.8-16.4 ng/g of *BaP*), Estuary and Western Xiamen Sea (4-25 ng/g of *Fl* and 8-163 ng/g of *BaP*).

The dominant origin of PAHs in sediment from the middle segment of the Yamuna River had a pyrogenic fingerprint that resulted from the incomplete combustion of fossil fuel and other organic materials. These combustion products enter the river from urban runoff, industrial discharges, and atmospheric input rather than from direct petroleum input. Terrestrial runoff is an important route of PAHs into the aquatic environment. Hoffman et al. (1984) compared urban runoff PAH inputs with other sources of PAHs to the upper Narragansett Bay and found that 71% of the higher molecular weight PAHs came from urban runoff, 10% from direct atmospheric fallout, and 18% from sewage treatment effluents. Therefore, terrestrial runoff may contribute large amounts of PAHs to aquatic sediments especially close to cities. It is possible, however, that the pyrogenic fingerprint can be so dominant that any petrogenic signal is undistinguishable, especially when low levels of petrogenic PAHs were present.

At ITO concentrations of Phen, Anth, *Fl*, Pyr, and *B[a]A* were found to be higher as compared to other sites moreover concentrations were higher during post-monsoon season. This could be due to post-monsoon depositions of PAHs in sediments as during monsoon storm event may result in rapid net deposition of sediment associated PAH adjacent to point of

input (Evans et al., 1990). According to the reviewed literature Phen is an indicator for the motor vehicle emissions and road particles. *Fl* and *Pyr* are considered typical pyrogenic products associated with incineration and oil combustion and are generated from high temperature condensation of low molecular weight compounds (Soclo et al., 2000). *Fl* is considered as a good pollution indicator in environments impacted by urban and industrial activities (Chaudhry, 1994). A dominance of *Pyr* over *Fl* is also clear from Fig 4.1. During the combustion process, *Pyr* is more stable than *Fl*, and hence pyrolytic products are usually characterized by a predominance of *Fl* over *Pyr* at ratios greater than one (Baumard et al., 1999).

*B[a]A* concentration was found to be highest at ITO of all the compounds analyzed. Because it is formed when gasoline, garbage, or any animal or plant material burns, it is usually found in smoke and soot. This chemical combines with dust particles in the air and is carried into water and soil and onto crops. *B(a)A* is also found in creosote. <http://www.nature.nps.gov/hazardssafety/toxic/benzoant.pdf>.

*Chry* concentration was observed to be higher at NGDS. *Chry* is generally believed to be an aromatic compound of natural origin. It is mainly derived from pentacyclic triterpenes such as a- and b-amyrins, which are major constituents of epicuticular waxes of terrestrial plants, through the processes of microbial degradation (Wakeham et al., 1980). Its higher concentration may indicate for coal combustion emission also.

Concentration of *B[b]F*, *B[k]F* and *DB[ah]A* was found to be higher at Okhla. *B[b]F* is most likely to result from the incomplete combustion of a variety of fuels including wood and fossil fuels. Plants may also produce *B[b]F*. *B[k]F* is an ubiquitous product of incomplete combustion. In air and water it is largely associated with particulate matter and its presence is greatest near sources, but *B[k]F* is reasonably stable in the atmosphere and capable of long distant transport. *DB[ah]A* is an ubiquitous product of incomplete combustion. It is largely associated with particulate matter, soils, and sediments. Its presence in places distant from primary sources indicates that it is reasonably stable in the atmosphere and capable of long distance transport. (<http://www.anr.state.vt.us/dec/wastediv/sms/Clarendon/Chemicals.found.presentation.text.doc>)

Spatial and seasonal variation of *B[a]P* concentration and its percentage are depicted in Fig 4.8 and 4.9. It is clear from the graph that except at RG, the percentage of *B[a]P* concentration at all sites was high during post-monsoon season while at RG, it is higher during pre-monsoon. During monsoon the percentage of *B[a]P* concentrations are comparatively lower at all the sites. During pre-monsoon *B[a]P* concentration at NGUS is minimum while at NGDS, ITO and OK shows almost same level of *B[a]P*. During monsoon also the trend is almost similar being slightly higher at ITO and OK. During post-monsoon concentrations show significant variation being highest at ITO and minimum at RG. From RG to ITO there is an increasing trend. Moreover the high vehicular traffic at ITO could be one of the major reasons for the high concentration of *B[a]P*. Burning of fossil fuels is an important source of PAHs in the environment. Significant quantities of benzo[a]pyrene and other PAHs have been identified in vehicular exhaust. Harrison et al. (1996) reported that in Birmingham, 88% of the concentration of *B[a]P* in air was mainly from road traffic emissions.

During non-monsoon (non-flood) periods, which account for all but 2 months of a year, flows are low to minimal and pollution is dominated by the in-stream uses, and point discharges from urban/industrial sources. The water quality alters according to the dilution available in the river. The pollution load added from Haryana in the river is also intermittent. As there is no release of fresh water from Wazirabad in the dry season, it is the Delhi sewage, which constitutes the flow in the river. The sewage, although increasing in quantity over a period of time has not changed the quality of the river water substantially because the flow is dominated preponderantly by the sewage without being diluted by river water. During the dry weather flow in the river Yamuna along Delhi is nearly zero. Pollution in the Yamuna cannot be controlled fully unless a minimum flow is maintained in the river.

Pollution due to agricultural water, either as wash-off or as seepage, appears to be rare during the 8-10 fair weather months. During monsoon season the major source of organic pollution is as industrial wastewater, runoff from garbage dumps and city streets carries litter, deposited particulate matter and chemicals, carbonized coal product spills where they are deposited gets its way into the aquatic environment in huge quantity. Since most of the

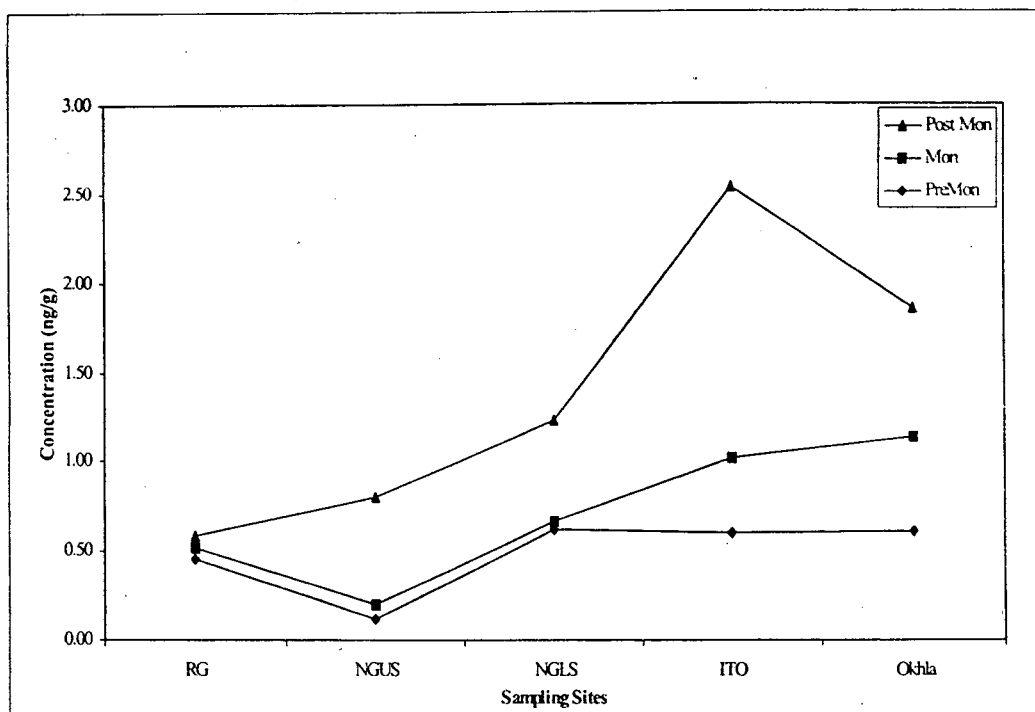


Fig. 4.8: Variation of B[a]P at different sites during Pre-monsoon, Monsoon and Post-Monsoon

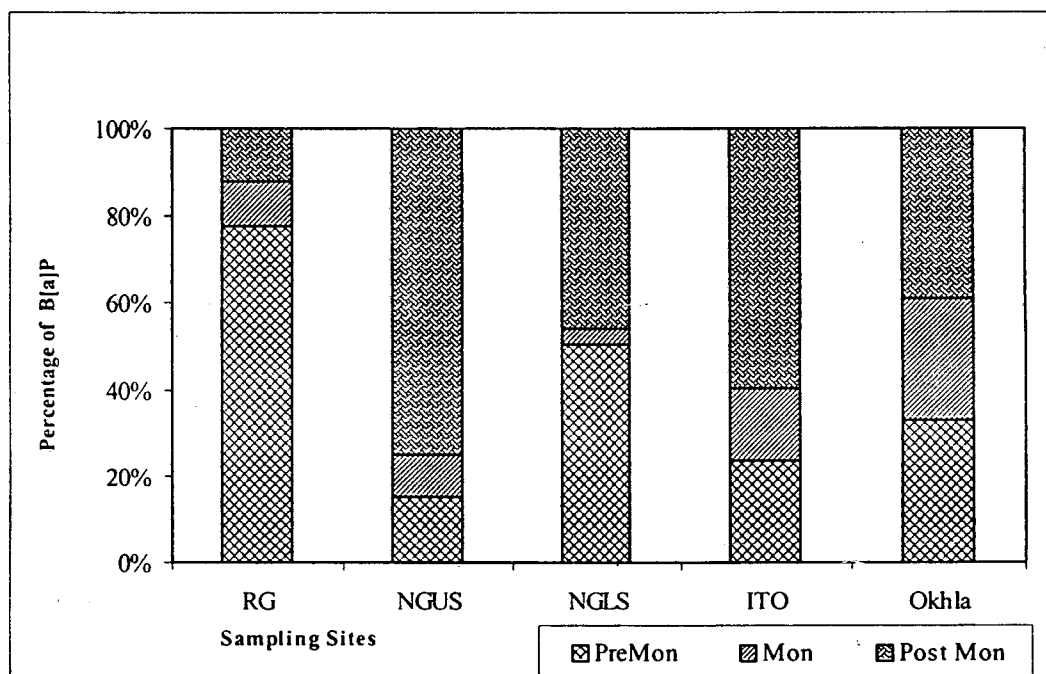


Fig. 4.9: Percentage variation of B[a]P at different sites during Pre-monsoon, Monsoon and Post-Monsoon



wastewater of these towns is discharged into the river without treatment and, the flow in the river at these places is too meagre to dilute the pollutant load. However due to the huge quantity of the water during monsoon the concentrated pollutant gets diluted, thereby leading to decreased levels during monsoon.

#### 4.3 Percentage Distribution

Percentage distribution of average concentrations of individual PAHs at all the five sites (Fig. 4.10-4.14) and of total concentration of individual PAHs are given in Fig. 5.15. PAH distribution at RG showed that *Fl* was the most abundant species (20.0%) followed by *Pyr*, *B[a]A*, *Anth*, *B[k]F*, *Phen*, *Chry*, *B[b]F*, *IP*, *B[a]P*, *B[ghi]P* and *DB[ah]A*.

At NGUS, *Pyr* and *B[a]A* were the most abundant compounds (16.0%), followed by *Fl*, *B[k]F*, *Anth* and *Chry*, *Phen* and *IP*, *DB[ah]A*, *B[a]P* and *B[ghi]P* and *B[k]F*.

At NGDS, *Chry* was the most abundant species (26.0%) followed by *Pyr*, *Fl*, *B[a]A* and *B[k]F*, *Anth*, *Phen*, *B[b]F*, *B[a]P* and *IP*, *B[ghi]P* & *DB[ah]A*.

At ITO, *B[a]A* (24%) was the most abundant species followed by *Pyr*, *Fl*, *Anth* and *Chry*, *B[k]F*, *Phen* and *B[a]P*, *B[b]F* & *DB[ah]A*, and *B[ghi]P* & *IP*.

At Okhla, the most abundant compound was *B[a]A* (16%) followed by *B[k]F*, *Fl*, *Pyr*, *DB[ah]A*, *B[ghi]P*, *Anth*, *IP*, *Chry*, *B[b]F* and *B[a]P*, and *Phen*.

Percentage of 3-, 4-, 5- and 6-ring in the sediments River Yamuna was plotted in Fig 4.16 (3-ring PAHs include *Phen* and *Anth*; 4-ring PAHs include *Fl*, *Pyr*, *B[a]A* and chrysene; 5-ring PAHs include *B[b]F*, *B[k]F*, *B[a]P* and *DB[a,h]A*; 6-ring PAHs include *IP* and *B[g,h,i]P*) at different site, which indicated that at all the sites 4 ring PAHs dominated followed by 5 ring, 3-ring and 6-ring PAH compounds. Together 4- and 5-ring PAHs accounted for more than half of total PAHs (up to 70%), while on average 3- and 6-ring PAHs occupied 29% of the total PAHs in sediment. Percentage of 4- and 5- ring compounds is maximum at ITO. The major sources could be combustion of coal and fossil fuels like petrol and diesel. The percentages of different ring compounds at all the sites were comparable. It indicates that at all the sites the sources of PAHs could be similar i.e. combustion.

Pereira et al. (1996) also showed that four-ring PAHs dominated PAH distributions in

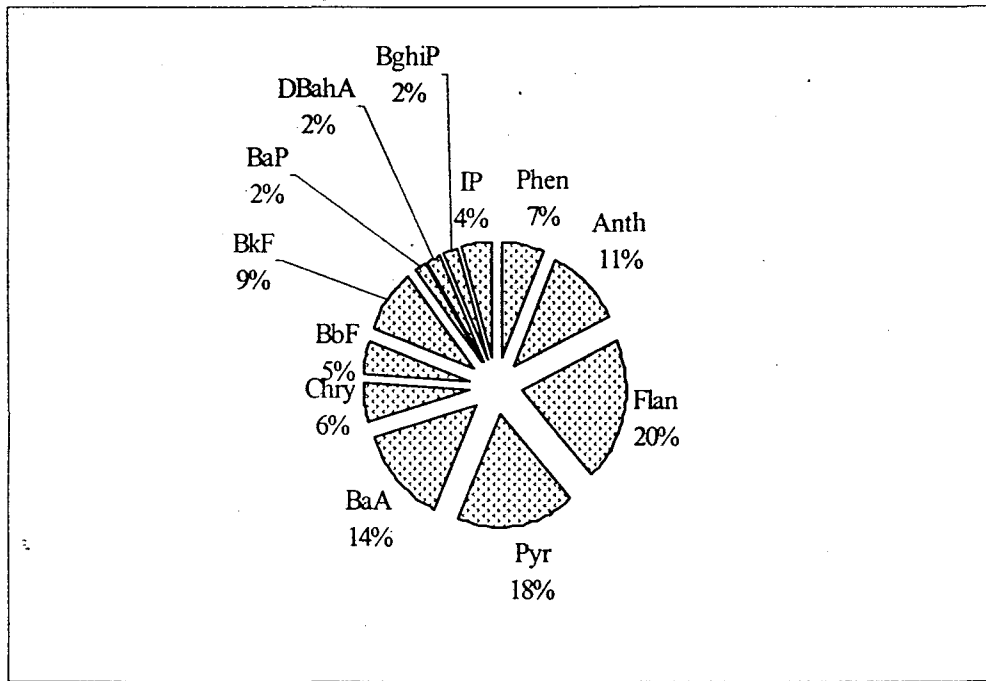


Fig. 4.10: Percentage distribution of individual PAHs at RG

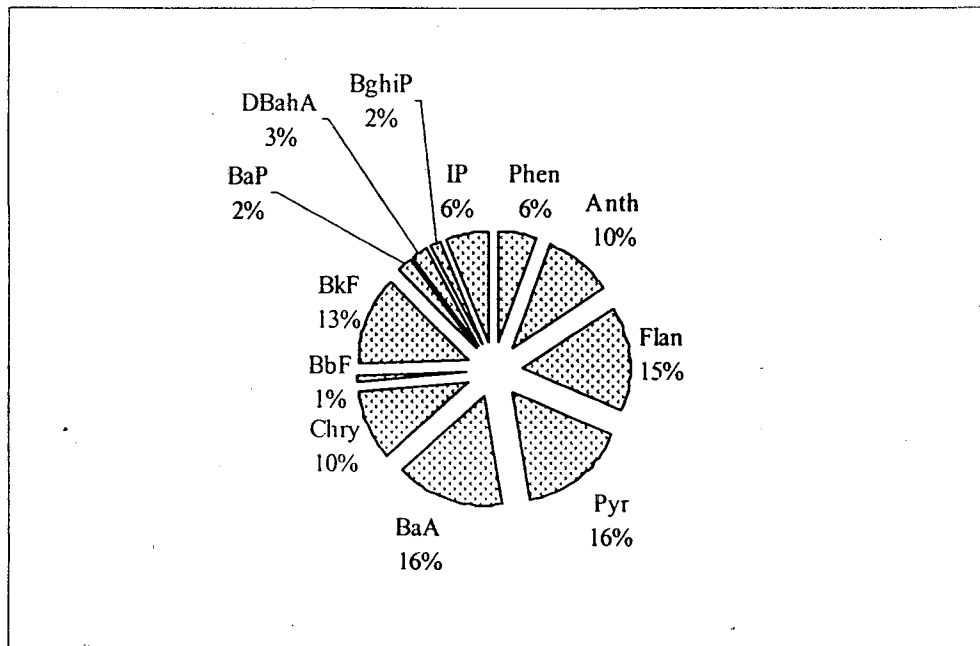


Fig. 4.11: Percentage distribution of individual PAHs at NGUS

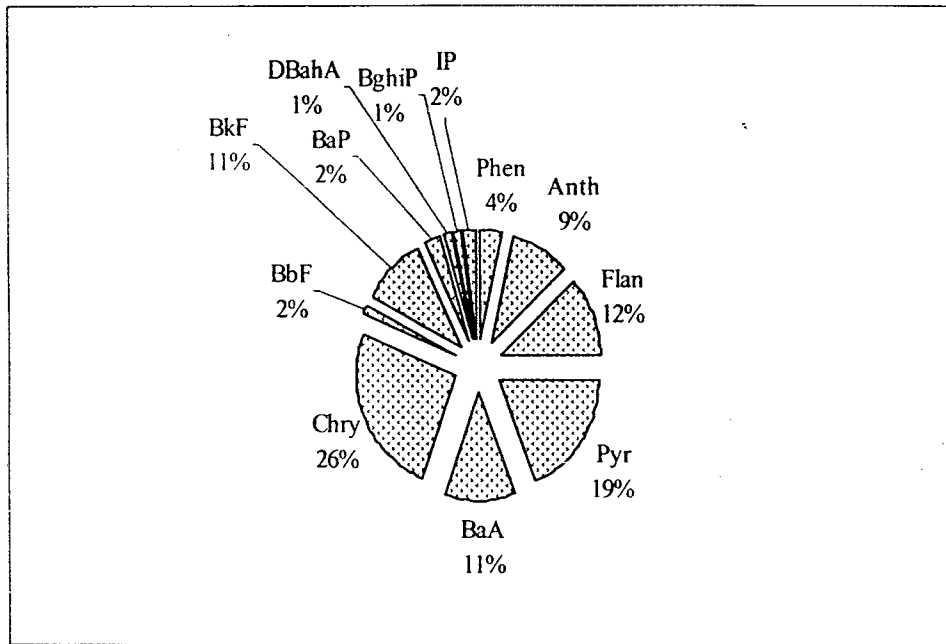


Fig. 4.12: Percentage distribution of individual PAHs at NGLS

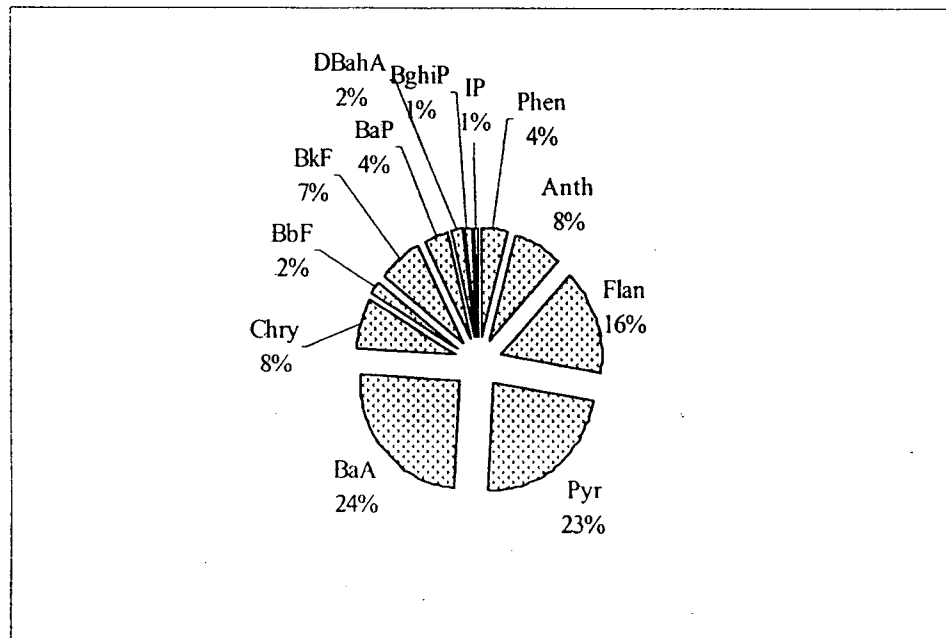
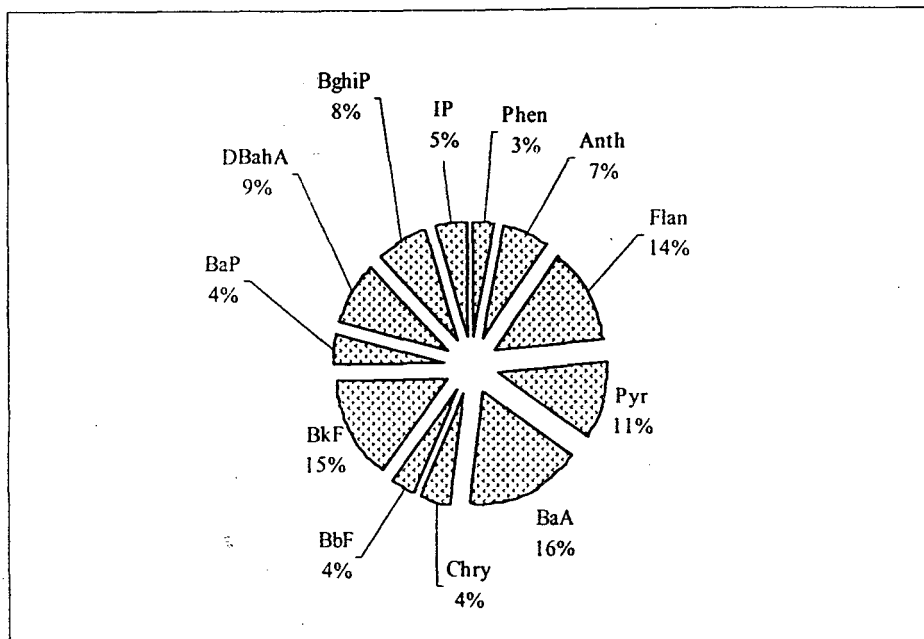
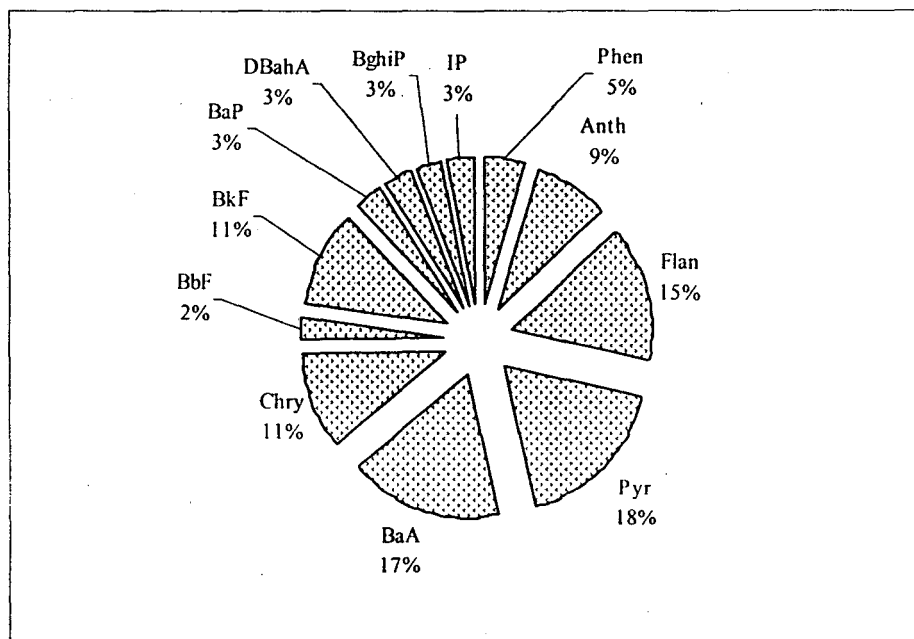


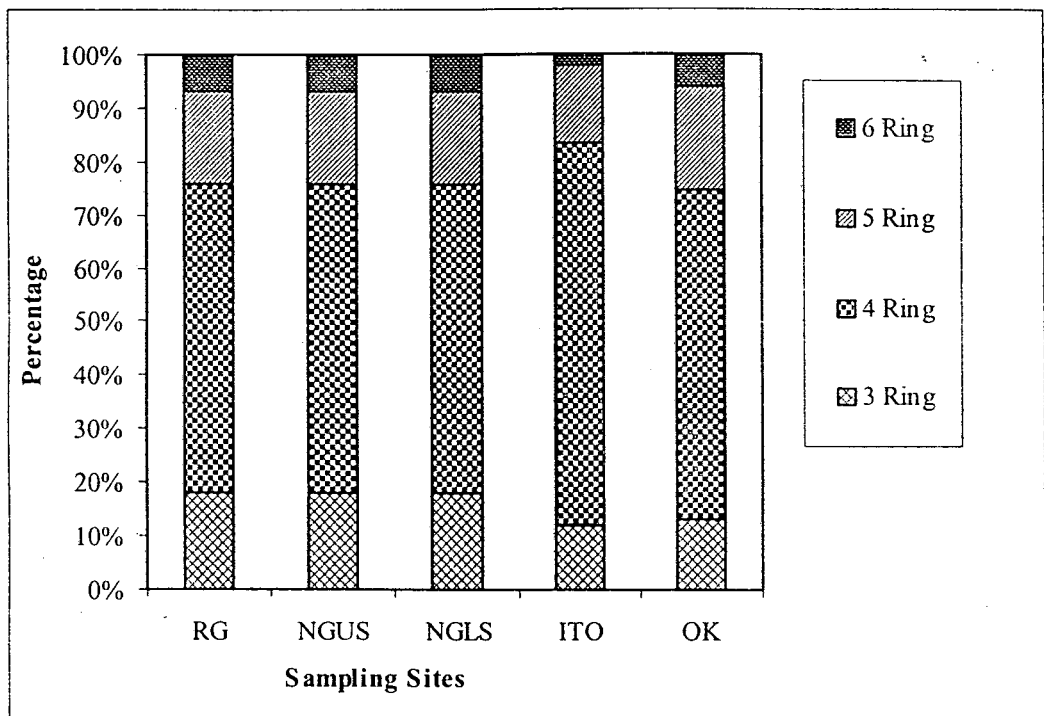
Fig. 4.13: Percentage distribution of individual PAHs at ITO



**Fig. 4.14:** Percentage distribution of individual PAHs at OK



**Fig. 4.15:** Average percentage (of all the sampling sites) distribution of individual PAHs



**Fig. 4.16:** Percentage composition of 3-, 4-, 5- and 6-ring PAHs in the Sediments of River Yamuna (3-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; 4-ring PAHs include Fl, Pyr, B[a]A and Chry; 5-ring PAHs include B[b]F, B[k]F, B[a]P and DB[ah]A; 6-ring PAHs include IP and B[ghi]P)

sediments from San Francisco Bay. Pyrolysis/ combustion of fossil materials yields such PAH assemblages, which are subsequently introduced into the aquatic environment by coastal and river runoff (Eganhouse et al., 1981; Hoffman et al., 1984) and by direct dry and wet precipitation from the atmosphere (Dickhut and Gustafson, 1995). Industrial and domestic wastes are often another important local source. The changes in the composition pattern of PAHs between sampling sites may occur due to variations in additional input sources (e.g. high or medium temperature combustion processes, different fossil materials).

An abundance of high molecular weight PAHs was also typically encountered in atmospheric particles and urban aerosols (Muel and Saguem, 1985; Sicre et al., 1987), due to their low water solubility, low microbial degradation rate (Readman et al., 1982) and high particulate affinity, compared with low molecular weight PAHs. Gschwend and Hites (1981) found that the relative abundances of individual PAHs were slightly altered by degradation during atmospheric transport to remote sites, but chemical and biological removal processes were unimportant once the PAHs were delivered to surface waters and sediment.

#### 4.4. Origin of the contamination-Sources

With the development of environmental geochemistry, some criteria, such as *Anth/178* and *B[a]A/228* ratio values, have been developed in order to distinguish between PAHs of various origins (Yunker et al., 2002). These criteria are based on peculiarities in PAH composition and distribution pattern as a function of the emission source. In the present study following four PAH isomer pair ratios were applied as distinct tracers to identify possible sources of PAH in sediments: anthracene/anthracene + phenanthrene (*Anth/178*); *B[a]A/ B[a]A + Chry (BaA/ 228)*; fluoranthene/fluoranthene + pyrene (*Fl/Fl + Pyr*); and Indeno[1,2,3-c,d]pyrene/Indeno[1,2,3-c,d]pyrene + Benzo[g,h,i]perylene (*IP/IP + B[ghi]P*).

The PAH isomer pair ratios determined from river sediment samples (given in Table 4.6) were compared to PAH isomer pair ratios determined from several major PAH sources (environmental samples, petroleum, and single-source combustion), which were compiled previously by Yunker et al. (2002) (Table 4.7 and 4.8). Additionally, for each sediment sample PAH isomer pair ratios, *Anth/178*, *BaA/228* and *IP/ IP + B[ghi]P* were plotted against *Fl/Fl +*

Table 4.6: PAHs isomer pair ratios at different sites

Sites	Anth/178	Fl/202	BaA/228	IP/IP+BghiP	Sites	Anth/178	Fl/202	BaA/228	IP/IP+BghiP	Sites	Anth/178	Fl/202	BaA/228	IP/IP+BghiP
RG	0.71	0.46	0.87	0.26	NGLS	0.75	0.33	0.44	0.39	Okh la	0.55	0.75	0.91	0.37
	0.73	0.46	0.86	0.24		0.74	0.33	0.44	0.36		0.55	0.76	0.92	0.36
	0.72	0.46	0.88	0.30		0.74	0.33	0.44	0.40		0.55	0.74	0.90	0.37
	0.32	0.55	0.55	0.38		0.55	0.48	0.52	0.40		0.67	0.31	0.71	0.33
	0.28	0.57	0.52	0.31		0.59	0.48	0.49	0.31		0.68	0.31	0.71	0.38
	0.33	0.55	0.50	0.49		0.61	0.51	0.50	0.45		0.67	0.33	0.70	0.00
	0.68	0.55	0.71	0.75		0.79	0.35	0.17	0.83		0.66	0.61	0.79	0.36
	0.74	0.54	0.72	0.80		0.84	0.32	0.19	0.74		0.72	0.59	0.79	0.41
	0.69	0.57	0.70	0.76		0.72	0.31	0.20	0.83		0.75	0.58	0.79	0.40
<b>Avg</b>	<b>0.58</b>	<b>0.52</b>	<b>0.70</b>	<b>0.48</b>	<b>Avg</b>	<b>0.70</b>	<b>0.38</b>	<b>0.38</b>	<b>0.52</b>	<b>Avg</b>	<b>0.65</b>	<b>0.55</b>	<b>0.80</b>	<b>0.33</b>
NGUS	0.68	0.63	0.76	0.94	ITO	0.63	0.60	0.67	0.25					
	0.63	0.64	0.75	0.95		0.62	0.55	0.68	0.52					
	0.64	0.67	0.76	0.92		0.64	0.65	0.66	0.32					
	0.28	0.47	0.54	0.35		0.70	0.54	0.55	0.32					
	0.27	0.45	0.54	1.00		0.69	0.56	0.56	0.00					
	0.30	0.47	0.55	1.00		0.71	0.55	0.57	0.31					
	0.75	0.33	0.54	0.35		0.59	0.23	0.87	0.36					
	0.73	0.33	0.56	0.31		0.59	0.31	0.83	0.33					
	0.75	0.33	0.52	0.33		0.60	0.36	0.80	0.33					
<b>Avg</b>	<b>0.56</b>	<b>0.48</b>	<b>0.61</b>	<b>0.68</b>	<b>Avg</b>	<b>0.64</b>	<b>0.48</b>	<b>0.69</b>	<b>0.30</b>					

Table 4.7

Possible PAH sources as determined from PAH isomer pair ratios

Sampling stations	An/178 <sup>a</sup>	Fl/Fl + Py <sup>a</sup>	BaA/228 <sup>a</sup>	IP/IP + BghiP <sup>a</sup>
RG	0.58(0.28-0.74)	0.52(0.46-0.57)	0.70(0.50-0.88)	0.48(0.24-0.80)
NGUS	0.50(0.27-0.75)	0.48(0.33-0.67)	0.61(0.52-0.76)	0.68(0.31-1.00)
NGDS	0.70(0.55-0.84)	0.38(0.31-0.51)	0.38(0.17-0.52)	0.52(0.31-0.83)
ITO	0.64(0.59-0.71)	0.48(0.23-0.65)	0.69(0.55-0.87)	0.30(0.00-0.36)
OK	0.65(0.55-0.75)	0.55(0.31-0.76)	0.80(0.70-0.92)	0.33(0.00-0.41)
PAH sources	An/178 <sup>b</sup>	Fl/Fl + Py <sup>b</sup>	BaA/228 <sup>b</sup>	IP/IP + BghiP <sup>b</sup>
<i>Petroleum/fossil fuels</i>				
Kerosene		0.46	0.35	0.48
Diesel oil	0.09 (0.03-0.17)	0.26 (0.01-0.47)	0.35 (0.12-0.71)	0.40 (0.25-0.65)
Crude oil		0.22 (0.14-0.26)		0.09
Shale oil	0.26	0.34	0.45	0.39
Lubricating oil		0.29		0.12 (0.00-0.13)
Coal	0.20 (0.00-0.41)			
Asphalt			0.50	0.52-0.54
<i>Combustion</i>				
Lignite and brown coal	0.08 (0.00-0.16)		0.44 (0.39-0.49)	0.57
Bituminous coal	0.33 (0.31-0.36)	0.53 (0.48-0.58)	0.34 (0.18-0.50)	0.48 (0.35-0.62)
Hard coal briquettes		0.57 (0.52-0.62)	0.43 (0.36-0.49)	0.52 (0.44-0.57)
Coal tar (SRM 1597)	0.18	0.58	0.54	0.53
Wood soot	0.26	0.50	0.43-0.49	0.55
Wood	0.19 (0.14-0.29)	0.51 (0.41-0.67)	0.46 (0.30-0.54)	0.54 (0.49-0.77)
Grasses	0.17 (0.13-0.23)	0.58 (0.53-0.63)	0.46 (0.44-0.49)	0.58 (0.52-0.69)
Gasoline	0.11	0.44	0.33-0.38	0.09-0.22
Kerosene	0.14 (0.12-0.16)	0.50	0.37 (0.30-0.44)	0.37
Diesel	0.11 (0.01-0.27)	0.39 (0.20-0.58)	0.38 (0.18-0.69)	0.35 (0.19-0.50)
No. 2 fuel oil		0.51 (0.47-0.55)		
Crude oil	0.22	0.44 (0.42-0.46)	0.49 (0.47-0.50)	0.47 (0.46-0.48)
<i>Environmental samples</i>				
Bush fire		0.61	0.23	0.70
Savanna fire particulate		0.59 (0.58-0.60)		0.39 (0.31-0.44)
Road dust	0.18	0.42		0.51
Lubricating oil, re-refined				0.36
Used engine oil, gasoline passenger car	0.22	0.30	0.50	0.18
Used engine oil, diesel car, truck and bus		0.37		0.29
Tunnel with light duty gasoline vehicles		0.45 (0.42-0.49)	0.46 (0.39-0.51)	0.30 (0.26-0.35)
Tunnel with heavy duty diesel trucks and gasoline vehicles		0.42 (0.41-0.44)	0.57 (0.53-0.60)	0.30 (0.24-0.40)
Roadway tunnels	0.13 (0.13-0.14)	0.43	0.42 (0.39-0.46)	0.30 (0.23-0.37)
Urban air (including SRM 1648 and 1649a)	0.08 (0.06-0.09)	0.56 (0.55-0.57)	0.30 (0.24-0.33)	0.40 (0.27-0.48)
Creosote treated wood piling	0.20 (0.16-0.26)	0.62 (0.61-0.64)	0.50 (0.46-0.53)	0.64 (0.59-0.68)

<sup>a</sup> PAH isomer pair ratios are the means and ranges (in parenthesis) for all the 1993-2001 sediment samples.<sup>b</sup> Means and/or ranges (in parenthesis) of PAH sources identified from Yunker et al. (2002).



F/Fl+Pyr	Combustion	Petroleum/fossil fuels	Environmental samples
0.52 (RG)	Bituminous coal 0.53 (0.48 – 0.58) Hard coal briquettes 0.52 (0.44 – 0.57) Coal tar (SRM 1597) 0.53 Wood soot 0.55 Wood 0.54 (0.49 – 0.77) Grasses 0.58 (0.52 – 0.69) Kerosene 0.39 (0.20 – 0.58) No. 2 fuel oil 0.51 (0.47 – 0.55)		Road dust 0.51
0.48 (NGUS, ITO)	Wood soot 0.50 Wood 0.51 (0.41 – 0.67) Gasoline 0.440 Kerosene 0.500 Diesel 0.39 (0.20 – 0.58) No. 2 fuel oil 0.51 (0.47 – 0.55) Crude oil 0.44 (0.42 – 0.46)	Kerosene 0.46 Diesel oil .26 (0.01 – 0.47)	Tunnel with light duty gasoline vehicles 0.45 (0.42 – 0.49)  Tunnel with heavy duty diesel trucks and gasoline vehicles 0.42 (0.41 – 0.44)
0.38 (NGLS)	Diesel 0.39 (0.20 – 0.58)		Used engine oil, diesel car, truck and bus 0.37
0.55 (Okhla)	Lignite and brown coal 0.53 (0.48 – 0.58) Bituminous coal 0.53 (0.48 – 0.58) Hard coal briquettes 0.52 (0.44 – 0.57) Coal tar (SRM 1597) 0.53 Wood soot .55 Wood .54 (0.49 – 0.77) Grasses 0.58 (0.52 – 0.69) Kerosene 0.39 (0.20 – 0.58) No. 2 fuel oil 0.51 (0.47 – 0.55)		Urban air (including SRM 1648 and 1649a) 0.56 (0.55 – 0.57)

Table 4.8 : Molecular pair ratios of *Fl/Fl+Pyr* at Different sites

BaA/228	Combustion	Petroleum/fossil fuels	Environmental samples
0.7 (RG)		Diesel oil 0.35 (0.12 – 0.71)	
0.61 (NGUS)		Diesel oil 0.35 (0.12 – 0.71)	Tunnel with heavy duty diesel trucks and gasoline vehicles 0.57 (0.53 – 0.60)
0.38 (NGLS)	Bituminous coal 0.34 (0.18 – 0.50) Hard coal briquettes 0.43 (0.36 – 0.49) Gasoline 0.33 – 0.38 Kerosene 0.37 (0.30 – 0.44) Diesel 0.38 (0.18 – 0.69)	Kerosene 0.35 Diesel oil 0.35 (0.12 – 0.71)	
0.69 (ITO)	Diesel 0.38 (0.18 – 0.69)	Diesel oil 0.35 (0.12 – 0.71)	
0.8 (Okhla)	Combustion		
IP/IP+BghiP	Combustion	Petroleum/fossil fuels	Environmental samples
0.48 (RG)	Kerosene 0.48 Diesel oil 0.40 (0.25 – 0.65) Bituminous coal 0.48 (0.35 – 0.62) Hard coal briquettes 0.52 (0.44 – 0.57) Diesel 0.35 (0.19 – 0.50) Crude oil 0.47 (0.46 – 0.48)		Urban air (including SRM 1648 and 1649a) 0.40 (0.27 – 0.48)
0.33 (NGUS)	Kerosene 0.37 Diesel 0.35 (0.19 – 0.50)		Tunnel with light duty gasoline vehicles 0.30 (0.26 – 0.35) Tunnel with heavy duty diesel trucks and gasoline vehicles 0.30 (0.24 – 0.40) Roadway tunnels 0.30 (0.23 – 0.37)
0.68 (NGLS)	Wood 0.54 (0.49 – 0.77) Grasses 0.58 (0.52 – 0.69)		Bush fire 0.70 Creosote treated wood piling 0.64 (0.59 – 0.68)
0.52 (ITO)	Bituminous coal 0.48 (0.35 – 0.62) Hard coal briquettes 0.52 (0.44 – 0.57) Coal tar (SRM 1597) 0.53 Wood soot 0.55 Wood 0.54 (0.49 – 0.77) Grasses 0.58 (0.52 – 0.69)	Diesel oil 0.35 (0.12 – 0.71) Asphalt 0.52 – 0.54	Road dust 0.51
0.3 (Okhla)			Used engine oil, diesel car, truck and bus 0.29 Tunnel with light duty gasoline vehicles 0.30 (0.26 – 0.35) Tunnel with heavy duty diesel trucks and gasoline vehicles 0.30 (0.24 – 0.40) Roadway tunnels 0.30 (0.23 – 0.37) Urban air (including SRM 1648 and 1649a) 0.40 (0.27 – 0.48)

Table 4.9 : Molecular pair ratios of BaA/228 and IP/IP+B[ghi]P at Different sites

*Pyr* to show how PAH distribute relative to their possible sources (Fig. 4.17, based on Yunker et al., 2002). Based on the PAH isomer pair ratio measurements compiled by Yunker et al. (2002): *Anth/178* ratio < 0.10 indicates dominance of petroleum and >0.10 indicates dominance of combustion; *Fl/Fl + Pyr* ratio < 0.40 petroleum, 0.40–0.50 petroleum combustion, and >0.50 combustion of coal, grasses and wood; *B[a]A/228* ratio < 0.20 petroleum, 0.20–0.35 petroleum and combustion, and >0.35 combustion; and *IP/IP + B[ghi]P* < 0.20 petroleum, 0.20–0.50 petroleum combustion, and >0.50 combustion of coal, grasses and wood.

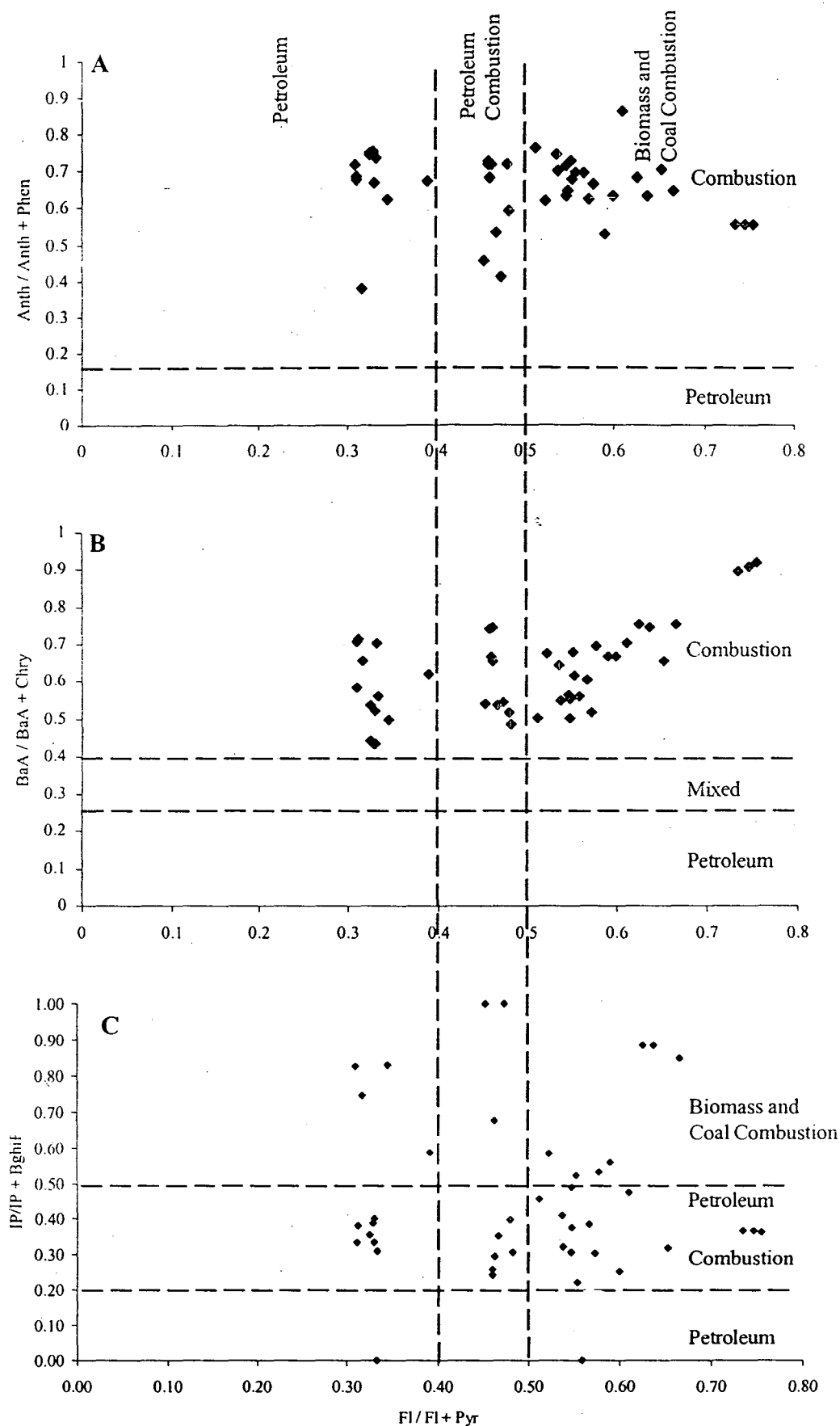
The PAH isomer pair ratios show that PAH in river sediments are derived primarily from combustion sources (Fig. 4.17). The possible major sources of combustion derived PAH include fossil fuels/petroleum (gasoline, crude oil, and coal) and biomass (wood and grasses). In addition, there are minor amounts of PAH that are possibly derived from direct input of unburned fossil fuels/petroleum (kerosene, shale oil, and coal). Several environmental samples that are also possible sources of PAH in sediments include used engine oil from gasoline passenger cars, air emissions collected from roadway tunnels with vehicular traffic, urban air and creosote-treated wood pilings.

*Anth/178* isomer pair ratio ranged from 0.28-0.74 at RG with a mean of 0.58, 0.27-0.75 with a mean of 0.50 at NGUS, 0.55-0.84 with a mean of 0.70 at NGDS, 0.59-0.71 at ITO with a mean of 0.64 and from 0.55-0.75 with a mean of 0.65 at Okhla. Average for all the sites was found to be 0.62 i.e. >0.10 at all the sites that indicates dominance of combustion.

*Fl/202* isomer pair ratio ranged from 0.46-0.57 at RG with a mean of 0.52, 0.33-0.67 with a mean of 0.48 at NGUS, 0.31-0.51 with a mean of 0.38 at NGDS, 0.23-0.65 at ITO with a mean of 0.48 and from 0.31-0.76 with a mean of 0.55 at Okhla. *B[a]A/228* isomer pair ratio ranged from 0.50-0.88 with a mean of 0.70 at RG, 0.52-0.76 with a mean of 0.61 at NGUS, 0.17-0.52 with a mean of 0.38 at NGDS, 0.55-0.87 with a mean of 0.69 at ITO and from 0.70-0.92 with a mean of 0.80 at Okhla.

*IP/IP+B[ghi]P* isomer pair ratio ranged from 0.24-0.80 with a mean of 0.48 at RG, 0.31-1.00 with a mean of 0.68 at NGUS, 0.31-0.83 with a mean of 0.52 at NGDS, 0.00-0.36 with a mean of 0.30 at ITO and from 0.00-0.41 with a mean of 0.33 at Okhla.

*Anth/178* isomer pair ratio shows a value of >0.10 throughout the river indicating



**Fig 4.17:** Plots of PAHs isomers pair ratios for source identification: (A) Anth/Anth+Phen Vs FI/FI+Pyr (B) BaA/BaA + Chry Vs FI/FI+Pyr (C) IP/IP + BghiP Vs FI/FI+Pyr. Isomer ratios were calculated for individual stations where possible, source boundary lines are based on Yunker et al., (2002)

combustion being the major source of PAHs.

The *Fl/Fl + Pyr* isomer pair ratios (Table 4.8) show that in the surficial sediment of river Yamuna, combustion of coal, coal tar, biomass, gasoline, kerosene, diesel, fuel oil, and crude oil (all segments of the river) are possible major sources of PAH. Unburned petroleum, specifically kerosene and diesel oil, are possible sources of PAH at NG and ITO, but only minor contributors. The *Fl/Fl + Pyr* isomer pair ratios closely match those determined from few (Benner et al., 1989; Fraser et al., 1998) environmental sources, which include a tunnel with light duty and heavy-duty diesel trucks (NGUS and ITO), used engine oil, diesel car, truck and bus (NGDS) and Urban air (including SRM 1648 and 1649a) (Okhla).

The *B[a]A/228* isomer pair ratios (Table 4.9) show that PAH are derived primarily from combustion with lower occurrences of PAH from mixed (combustion and petroleum) sources (Fig. 4.17). Combustion of diesel, kerosene, gasoline (at all the sites) and coal (NGDS and Okhla) is possible major sources of PAH in sediments. Unburned petroleum, specifically kerosene and diesel oil, are possible sources of PAH at all the stations except Okhla, but only minor contributors. The *B[a]A/228* isomer ratios for the samples closely match those determined from environmental samples that include a tunnel with heavy-duty diesel trucks and gasoline vehicles (NGUS).

The *IP/IP + B[ghi]P* isomer pair ratios (Table 4.9) show that PAH are derived primarily from biomass and coal combustion with a lower occurrence of PAH derived petroleum combustion (kerosene and diesel), and petroleum (diesel and asphalt) (Fig. 4.17). Combustion of biomass and coal are possible major sources of PAH at ITO, NGDS and Okhla, combustion of diesel and kerosene are major sources at NGUS while at RG it represents mixed sources. Unburned petroleum in the diesel oil and asphalt range is found at ITO (Table 4.8). Diesel can enter the river primarily through storm water runoff following release from diesel-powered vehicles and machinery. The *IP/IP + B[ghi]P* isomer ratios for the samples closely match those determined from environmental samples that include urban air, roadways tunnel, a tunnel with light duty and heavy duty diesel trucks (Okhla, NGUS), road dust (ITO), urban air (RG) and creosote treated wood piling, bush fire (NGDS).

Although distinct sources can be inferred from PAH isomer pair ratios, it is well

documented that in urban areas PAH can originate from a variety of sources and be transported by different pathways. The wide ranges of the PAH isomer pair ratios found in river sediments show that a unique source's PAH signature could be altered by biological (e.g., bacterial degradation), chemical (e.g., oxidation and reduction), and physical (e.g., air mass mixing and sediment re-suspension) processes during transport and after deposition into sediments.

*Conclusions*

## CONCLUSIONS

- $\Sigma_{12}$ PAH concentrations were ranged from 10.59-20.94 ng/g, being maximum at ITO that ranged from 10.81-47.83 ng/g with a mean of  $20.94 \pm 13.60$  and minimum at RG with the concentration range 8.45-14.44 with a mean of  $10.59 \pm 2.89$  ng/g.
- At all the sites  $\Sigma_{12}$ PAH concentrations were observed to be minimum during monsoon while followed an increasing trend was observed from pre- to post-monsoon season.
- At ITO *Phen*, *Anth*, *Fl*, *Pyr*, and *B[a]A* dominated, while at NGLS *Chry* was an abundant species. At OK, *B[k]F*, *DB[a,h]A*, and *B[g,h,i]P* were observed to be very high, while at RG and Okhla *B[b]F* was present in comparable amounts and *IP* concentrations were comparable at NGUS and Okhla.
- From RG to ITO, *B[a]P* concentration showed an increasing trend and at Okhla it was lower than the concentration at ITO, which followed the same trend as of  $\Sigma_{12}$  PAH concentration.
- Among the PAHs analyzed the proportion of 4- ring compounds were dominated at all the sites and 3, 4, and 5 – ring compounds together accounted for 80-90% of total PAHs. The proportion of 3, 4, 5 and 6-ring PAHs didn't show significant variation at different sites.
- Percentage distribution of individual compounds in total PAHs concentration (taking all sites together) dominated by *Pyr* (18%). Percentage wise at RG, *FL* was in abundance (20%); at NGUS, *B[a]A* (16%) and *Pyr* (16%) dominated; at NGDS, *Chry* (26%) showed an abundance while at ITO (24%) and Okhla (16%) *B[a]A* dominated.
- The preliminary results that combustion could be the major contributing source to PAH load in Yamuna river sediments.
- In our study the concentration of PAHs were found to be lower as compared to the concentration reported in river sediments from other countries.
- In order to have a comprehensive picture of PAH sources and their seasonal variation in Yamuna rivers sediments a detailed study is required.



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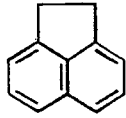
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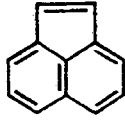
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## Annexure I

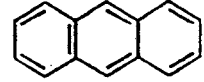
### Structure of the PAHs



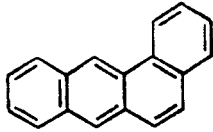
Acenaphthene



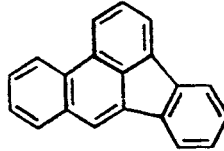
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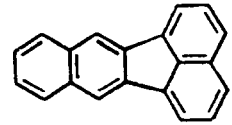
Anthracene



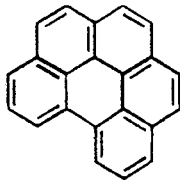
Benz(a)Anthracene



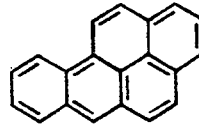
Benz(b)Fluoranthene



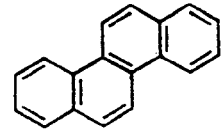
Benz(k)Fluoranthene



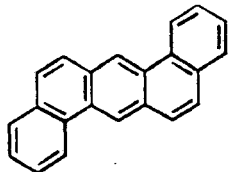
Benz(ghi)Perylene



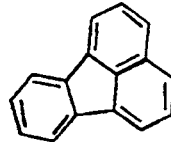
Benz(a)Pyrene



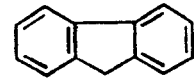
Chrysene



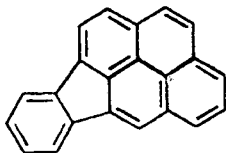
Dibenz(a,h)Anthracene



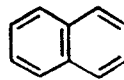
Fluoranthene



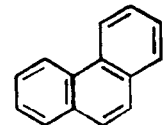
Fluorene



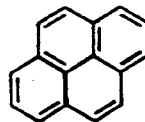
Indeno(1,2,3-cd)Pyrene



Naphthelene



Phenanthrene

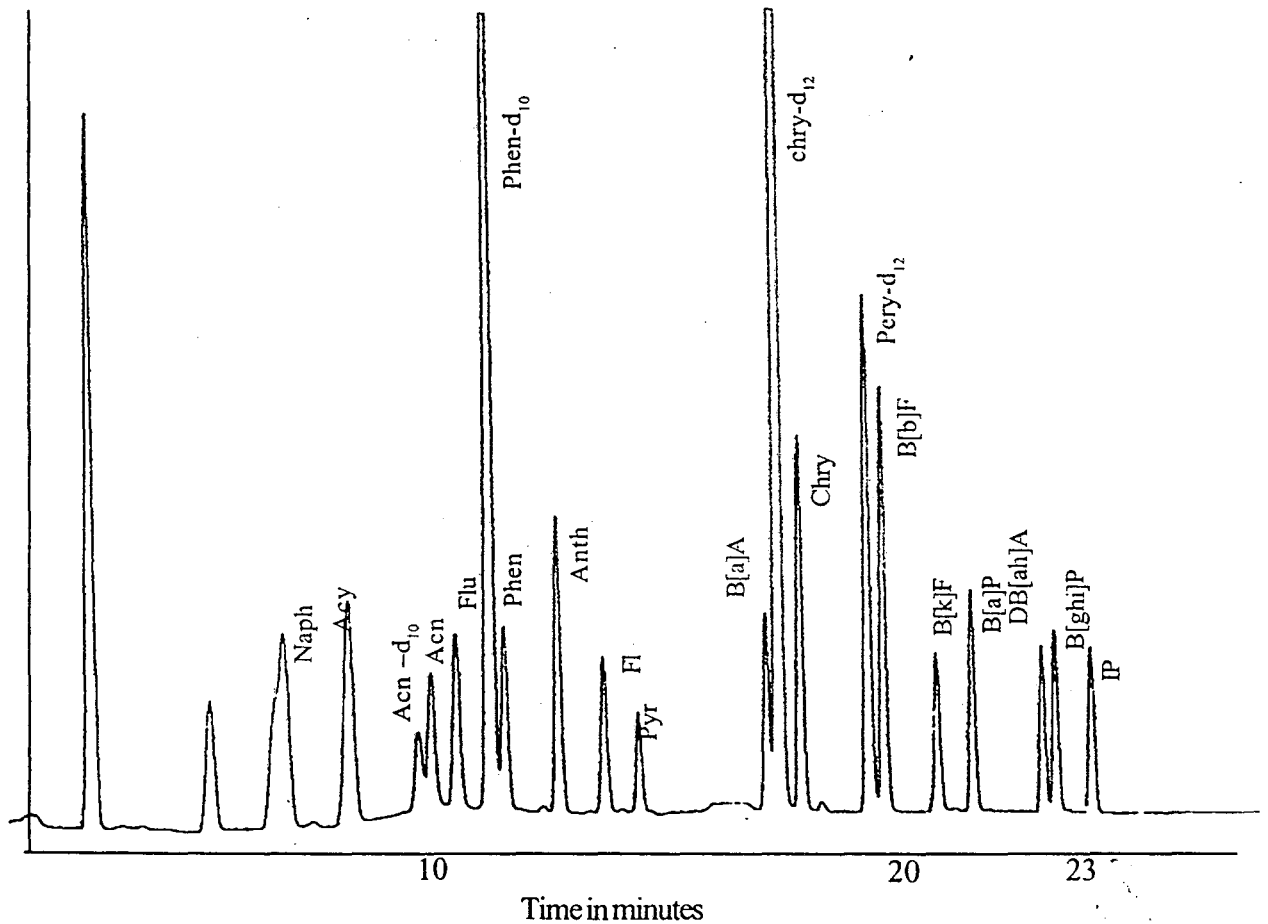


Pyrene

## Annexure II

### Chromatographic Conditions

5 min 50%/50% acetonitrile/water  
 20 min 100% acetonitrile  
 28 min 100% acetonitrile  
 32 min 50%/50% acetonitrile/water



HPLC chromatogram of an external standard solution (5ppm) spiked with internal standard solution (0.5ppm)

Analysed PAH and their corresponding Retention Times (min)

PAHs	RT Values	PAHs	RT Values
Naph	7.39	B[a]A	17.17
Acy	8.70	D <sub>12</sub> Chry	17.39
D <sub>10</sub> Acn	10.12	Chry	17.85
Acn	10.38	D <sub>12</sub> Pery	19.19
Flu	10.90	B[b]F	19.50
D <sub>10</sub> Phen	11.58	B[k]F	20.55
Phen	11.88	B[a]P	21.27
Anth	12.97	DB[ah]A	22.65
Fl	13.89	B[ghi]P	22.90
Pyr	14.58	IP	23.62

