

**DISTRIBUTION OF POLYCYCLIC AROMATIC  
HYDROCARBONS IN SOIL AROUND THE  
INTERNATIONAL AIRPORT IN DELHI**

Dissertation submitted to  
Jawaharlal Nehru University  
in partial fulfillment of the requirement for the award of the  
Degree of

**MASTER OF PHILOSOPHY**

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July 2006



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CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled "*Distribution of Polycyclic Aromatic Hydrocarbons in Soil around the International Airport in Delhi*" 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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"A hundred times a day I remind myself that my inner and outer life depends on the labours of other men, living and dead, and that I must exert myself in order to give in the full measure I have received and am still receiving."

Albert Einstein

## ACKNOWLEDGEMENT

*I express my sincere and deep sense of gratitude to Dr. P.S. Khillare for his valuable guidance, motivation and support in offering his scholastic supervision towards the successful completion of this work.*

*I extend my gratitude also to Prof. D.K. Banerjee for extending his lab facilities, the ex Dean, School of Environmental Sciences, Prof. J. Behari and present Dean, Prof. V.K. Jain for providing me the necessary facilities to carry out my research work.*

*I wish to express my special thanks to Ms. Tripti Agarwal for her valuable support and help during the entire sampling, analysis process and interpretation processes, which helped me to pursue this research work. I would like to especially mention about her positive attitude, which helped me to tackle difficult circumstances.*

*I would like to extend my heartfelt thanks to my senior Mr. Vijay Shridhar and for his constructive suggestions, support and friendly help during the entire M.Phil process. I would also like to thank Ms. Puneeta Pandey for her much needed help.*

*I wish to especially thank my friend, Vijay Kumar Chaurasia for his continuous help during the process of sampling.*

*I would like to acknowledge Tanushree Ma'am, Anjali Ma'am, Gurmeet Sir and Pawan Sir for their constant help, support and encouragement.*

*My sincere gratitude to Mr. B.D. Sharma and Mr. P.D. Gaikwad (In-charge CIF, SES) for their kind co-operation and technical assistance. Mr. Hoshiar Singh is duly acknowledged for his lab assistance.*

*I would like to extend my heartfelt thanks to all the faculty members and staff members of School of Environmental Sciences for their kind support during the study period.*

*My heartfelt thanks to my friends Akanksha, Chaudhuri, Kavinder, Kushagra, Manoj Rai, Parijat, Pradip, Rajesh, Shibaji, Sudarshana, Swati (CSRD) and Vishwamohan (of Jawaharlal Nehru University) and Daipayan, Dolon and Niladri(of Jadavpur University)for their every needed support to complete this work.*

*No written acknowledgement can express my thanks to my "Enemy Boss" and my "Ghulam" for tolerating my choleric mood swings, providing tension relieving talks and for their crisis management skills during difficult times.*

*Words might not suffice to express my thanks to Baba, Ma and Didi, without their faith in my abilities, constant encouragement and help to pursue higher studies, this work would not have been successful. I hope I have been able to partially fulfil their dreams. Last, but not the least, it would be unfair not to mention Molly, whose naughty innocence inspired me more than anything else.*

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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

*Flan* = Fluoranthene

*Flu* = Fluorene

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

*Naph* = Naphthalene

*Phen* = Phenanthrene

*Pyr* = Pyrene



# *Chapter I*

## *Introduction*

Airports are characterized under the U.S. EPA "National Air Toxics Program" as an example of complex facilities that produce HAPs (Hazardous air pollutants), from multiple sources ([www.ipcc-hggip.iges.or.jp](http://www.ipcc-hggip.iges.or.jp)). Organic HAPs are typically trace species formed from carbon fragments during combustion; however, they are of significant environmental concerns due to their highly toxic and mutagenic properties ([www.aeee.net](http://www.aeee.net)). The U. S. EPA has listed 14 HAPs, they believe are present in the exhaust of aircraft and/or their ground support equipment (GSE), which included a group of 16 PAHs, as Polycyclic Organic Matter (POM) (URS Corporation for Federal Aviation Administration, Office of Environment and Energy, 2003). Aircraft hydrocarbon emissions rank as the eleventh highest annual emission contributor in comparison with the top 60 source categories in the United States (U.S. EPA, 1977). On a regional scale, airports contribute upto 3% of the total annual emission to the surrounding urban areas (Cirillo et al., 1975; Jordan, 1977), but in rural areas an airport may represent the largest single contributor of total emissions in its area of air quality influence (Yamartino et al., 1980). Neither aircraft nor airports meet the definitions of the source types that are under section 112 of Clean Air Act (CAA, USA), nor are they specifically listed among the source types that are regulated. Current Federal Air Act (FAA) guidelines pertaining to air quality do not specifically address HAPs. Most monitoring efforts have thus far been relatively short-term (i.e. 3 days to a few weeks) and there have been no long term or permanent programs conducted (URS Corporation for Federal Aviation Administration, Office of Environment and Energy, 2003).

Aircraft engines (piston and turbine) have been demonstrated to emit considerable amounts of carcinogenic hydrocarbon, benzo(a)pyrene (2-10 mg/minute), associated with particulates. Benzo(a)pyrene has been found in soil and vegetation samples (Shabad and Smirnov, 1972). Other particulate-

associated polycyclic aromatic hydrocarbons are also emitted from aircraft. (Robertson et al., 1980) and as a class of compounds, represent a source of carcinogenic pollution. Measurement studies have confirmed that airports contribute significantly to hydrocarbon concentrations in the vicinity (Clark et al., 1983).

Most PAHs reach the soil via deposition from the atmosphere. The flux of PAHs to soil is largely influenced by their concentrations in the atmosphere (Wilcke et al., 1996). Gaseous and particle-bound PAHs can be transported over long distances before deposition (Skrbic et al., 2005). PAHs are strongly adsorbed to the organic fraction of soils, considered as the main sinks for PAHs in the environment (Garcia-Alonso, et al., 2003). Soils account for 90% of total PAH environmental burden (Wu et al., 2005). 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 organic pollutants usually occur close to point sources, although long-range atmospheric transport and subsequent deposition have led to significant environmental accumulation (Garcia-Alonso et al., 2003). US Environmental Protection Agency (EPA) has fixed 16 PAHs as priority pollutants, the latest being effective from 1997 (US EPA, 1997). 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. The best-known model compound from this group is highly carcinogenic Benzo(a)pyrene (*B(a)P*). PAHs generally occur as complex mixtures and not as single compounds in urban area environmental samples (Wu et al., 2005).

## 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 and structures are given in Table 1.1 and Appendix I respectively. 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 orders 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 between gas and particle phase (Lane, 1989).

PAHs are non-polar organic hydrocarbons. Aqueous solubilities of PAHs 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

**Table 1.1. Physical and chemical properties of PAHs**

Compounds	Mol. Wt	Abbr.	Mol. Formula	Melting point (°C)	Boiling Poir (°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
Napthelene	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	- <sup>2</sup>
Chrysene	228	Chry	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)

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 quinines 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 PAH losses during the 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; Prah1 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 (Prah1 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 soil 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). The derivatives from biogenic precursors like terpenes, pigments and steroids are also the important PAHs composition in marine environment (Wakeham et al., 1980; Budzinski et al., 1997). Indeed, PAHs can be produced from the short-term degradation of biogenic precursors (Baumard et al., 1998).

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). 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 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 contain 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 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, 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 soil environment by dry deposition of airborne particulate matter, or wet deposition by rainfall (Wu et al., 2005). PAHs with three or more rings tend to be strongly adsorbed onto the soils.

Strong sorption, leaching coupled with very low water solubility and very low pressures make leaching and volatilization insignificant pathway of PAH dissipation (Park et al., 1990).

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). Because PAH are minor components in petroleum, diesel and aviation fuels, PAHs can be introduced into the soil through combustion, and engine emissions (PAH position paper, 2001). Additionally, PAH can enter the water column through urban runoff (Hoffman et al., 1984). Once in the water column, these dissolved PAH bind to suspended particulate matter due to their hydrophobic properties and can be transported to the urban surface soils. Soils 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 soil PAH in locations close to centers of human activity (Yang et al., 1991; Wang et al., 2004; Skrbic, et al., 2005).

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, sediments and soils 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). 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 through volatilization (McVeety and Hites, 1988).

### **1.5 Soil as a sink for PAHs**

PAHs belong to the semi-volatile organic contaminant class and occur in the atmosphere under gaseous and particulate phases. Gaseous and particle-bound PAHs can be transported over long distances before deposition (Skrbic et al., 2005). Air borne particles may be delivered to surfaces by wet and dry depositions. Several transport mechanisms, such as turbulent diffusion, precipitation, sedimentation, Brownian diffusion, interception and inertial migration influence the dry deposition process of airborne particles. Large particles ( $d > 10\mu\text{m}$ ) are transported mainly by sedimentation; hence the large particulate PAHs tend to be deposited near the urban setting. Small particles ( $d < 1\mu\text{m}$ ) which behave like gases are often transported and deposited far away from the urban setting, where they originated (Baek et al., 1991).

Most PAHs reach the soil via deposition from the atmosphere. Wild and Jones (1995) estimated emissions of 11 PAHs to the UK atmosphere to total about 700 t/a and the average deposition rate to be 8.4 g/ha/a. The flux of PAHs to soil is largely influenced by their concentrations in the atmosphere (Wilcke, 2000).

It is estimated that more than 90% of the total burden of PAHs resides in the subsurface soils, though soil profile data show that these pollutants may extend into much deeper layers. The main cause of contamination of the terrestrial environment with PAHs is atmospheric deposition, although only a fraction of it is deposited directly on the soil, whereas the other part is initially

has also been observed in studies investigating PAH concentrations in soils depending on the proximity to the source (Nadal et al., 2004).

Strong sorption coupled with very low water solubility and very low vapor pressures make leaching and volatilization insignificant pathway of PAHs dissipation. Also plants hardly take up any PAHs from soil. PAHs are quite resistant to degradation, but soil bacteria are the primary degraders of PAHs in soil. PAHs with three and more rings tend to be strongly adsorbed to the soil. The range of half-lives for PAH in soil estimated by researchers is quite large. They vary dependent on the compound, from 2 month to 2 years and from 8 to 28 years (Skrbic et al., 2005).

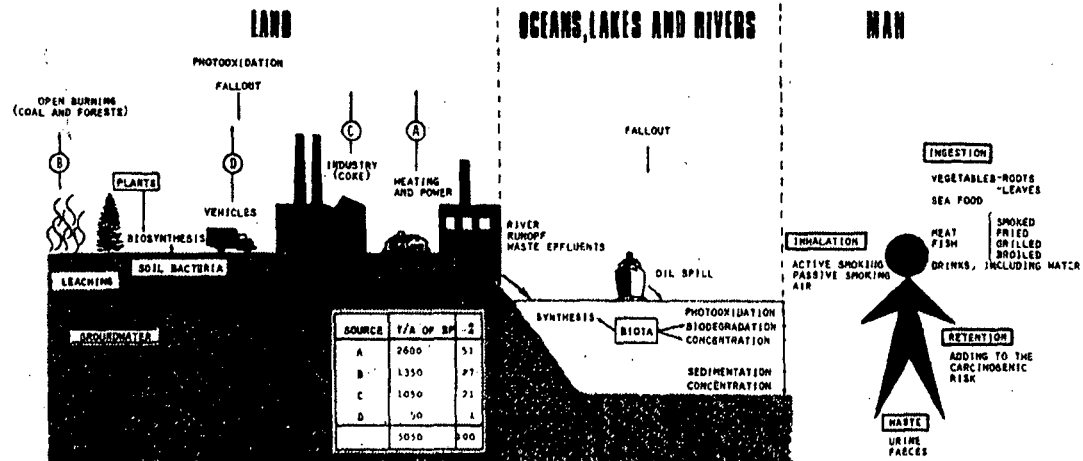
Because PAHs are lipophilic, their deposition on soil and surface waters may also lead to bio-accumulation within the food chain (Bakkera et al., 2000). Human exposure to PAHs (non-smokers) through food is found to be maximum, 93% of total, while through soil (accidental ingestion) it is found to be 1.9%. This accumulation process may cause indirect exposure of humans to PAHs, many of which are carcinogens or mutagens, through the consumption of fruits and vegetables. High content of PAHs in agricultural soils may not only create a risk to humans through the introduction of these pollutants into the food chains, but also affect the habitat function of soils, which is the basis for the yield of agricultural products (Maliszewska-Kordybach and Smreczak, 2000).

Since environmental contamination by PAHs presents a risk both to human health and biosystems mainly due to their potentially toxic, carcinogenic, and mutagenic effects on animals and human beings, USEPA has identified 16 PAHs as "priority pollutants" (Skrbic et al., 2005). These organic contaminants have the potential to manifest ecotoxicological activity. Although POPs are truly multimedia contaminants of the environment, the majority of them finally concentrate in soils (Maliszewska-Kordybach and Smreczak, 2000).

## 1.6 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 showed 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 (Shabad, 1980). 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 biomagnifications up the food chain is not likely to be a factor because high trophic level consumers, such as humans, can metabolize these substances.

Fig 1.1. PAHs cycle in Environment



The environmental cycle of PAH.

### **1.7 Significance of the study**

There are 126 airports in India (The Financial Express, 22 Feb, 2006), and around 80 airports are in cities with populations of more than 0.1 million. Before open sky policy India had only two airlines, Air India and Indian Airlines as international and domestic airlines respectively. But nowadays, the number of domestic carriers is growing, e.g. Jet Airways, Air Deccan, Spice Jet, Air Sahara and Kingfisher Airlines. At Delhi alone, daily 230 domestic aircrafts land and take-off. This means that over 4.8 million passengers are ferried by private airlines alone every year (Hindustan Times, 4 Feb, 2006) Due to development of airports in small towns and non-metros, e.g. Ahmedabad, Amritsar, Guwahati and increase in tourism in India, there is an increase in the number of flights. Thus the quantity of air pollutants due to exponential growth in the airlines business is increasing and as a result the deposition of these air pollutants in the soil around the airports is extremely detrimental causing soil pollution. Knowledge of soil contamination with PAH is needed to avoid exposure to the residents around the airport site, to prevent food production risk through the entry of PAHs from air, soil and water and ultimately into the food chain and to restrict the deleterious effect of these contaminants on the soil ecosystem. The environmental legislation in India does not quantitatively regulate their occurrence in soil. PAH concentrations in the soil of Indian airports have never been studied and the extent of soil pollution around the airport remains unknown. Since aviation affects the environment both globally and locally in a negative sense and consequently also has negative impacts on health, striking a balance between environmental impact, economic growth and social development is essential.

The objectives of the present study was to obtain reliable measurements in the surface soil, to study seasonal variations and to identify the main sources of PAHs around the airport, so that urban soil in the vicinity of the IGI Airport can

be characterized in terms of the selected PAH concentration and effective soil standards for PAH can be developed.



*Chapter II*

*Literature Review*

As a result of the environmental importance and the heightened awareness about the biochemical and toxicological roles of Polycyclic Aromatic Hydrocarbons (PAHs) in man and animals, these compounds have been studied extensively in different environmental matrices 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 (Shabad and Smirnov, 1972; Maliszewska-Kordybach, 1996; and Ducoulombier and Rychen, 2003).

The widespread distribution of soil 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 soil PAH data have been acquired in recent years from a small range of tropical/subtropical regions in Asia (Spitzer and Kuwatsuka, 1993; Nam et al., 2003; Tao et al., 2004; Chen et al., 2005 and Ma et al., 2005) and much lesser work has been done on PAHs in airport soils (Shabad and Smirnov, 1972; Ducoulombier and Rychen, 2003).

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 (Macias-Zamora et al., 2002).

### **2.1 Emissions from Jet Fuels**

The aviation jet fuel widely used in turbine engine aircraft is manufactured from straight-run kerosene. The combustion quality of jet fuel is largely related to the hydrocarbon composition of the fuel itself; paraffins have better burning properties than aromatic compounds, especially naphthalenes and light polycyclic aromatic hydrocarbons (PAHs), which are characterized as soot and smoke producers (Bernabei et al., 2003).

Aviation turbine fuels (jet fuels) are similar to other petroleum products that have a boiling range of approximately 300F to 550F. Kerosene and No.1 grades of fuel oil and diesel, and gas turbine oil share many similar physical and chemical properties with jet fuel. Civilian aircraft primarily use Jet A or Jet A-1 fuel. Military aircraft use JP-5 or JP-8 fuel (White and Russell, 1999).

The primary ingredient of both JP-5 and JP-8 is kerosene and the composition of these fuels is basically same as kerosene, with the exception that various additives are not found in kerosene. Typical additives to JP-5 and JP-8 include anti-oxidants (including phenolic antioxidants), static inhibitor, corrosion inhibitor, fuel system icing inhibitor, lubrication improvers, biocides and thermal stability improvers (Shumway, 2000). Emissions from combustion of aviation fuels might lead to pollution around different airports.

### **2.2 Emissions at different airports**

Neither aircraft nor airports meet the definitions of the source types that are under section 112 of Clean Air Act (CAA, USA), nor are they specifically listed among the source types that are regulated. Current Federal Air Act (FAA) guidelines pertaining to air quality do not specifically address HAPs. Most monitoring efforts

have thus far been relatively short-term (i.e. 3 days to a few weeks) and there have been no long term or permanent programs conducted.

In a study conducted at monitoring sites located adjacent to the Los Angeles International Airport, revealed that levels of both soot particles and elemental carbon (products of incomplete fuel combustion) were higher when compared to other off-site locations.

Assessment of air quality impacts associated with Chicago O'Hare International Airport showed that based on monitoring data collected both upwind and downwind of the airport, the results concluded that Hazardous Air Pollutants (HAPs) originating at the airport were migrating across the fenceline into residential areas.

IEPA, 2002 (Illinois Environmental Protection Agency) concluded that while downwind levels of HAPs were higher, they were comparable to other sites located away from airport and well within the range of levels considered "typical" of an urban environment.

Sampling of HAPs in the vicinity of Teterboro Airport in New Jersey (Environ, 2001) concluded that concentrations of HAPs adjacent to the airport were higher in comparison to the state site.

At Charlotte/Douglas International Airport revealed that jet fuel indicators were not found in samples collected and that regional emissions of these pollutants are more likely the source, both on and off the airport.

Seattle-Tacoma International Airport monitoring results indicate that the highest HAP levels occur on the airport, but that off-site and down-wind measurements were not easily differentiated, nor were the levels significantly different from levels found in other urban areas.

Measurements around Hamburg Airport show no elevated levels of PAHs. At Amsterdam Schipol Airport Volatile Organic Compounds (VOC) concentrations

were not significantly different than those measured elsewhere in the urban airshed; and at Gatwick International Airport near London, hydrocarbon concentrations were reported to much lower when compared to a central London site. (URS Corporation for Federal Aviation Administration, Office of Environment and Energy, 2003). Two areas exist where aircraft engine emissions might be a problem: the environment in and around the airport and the stratosphere (Thomas, 1989).

Aircraft-Related HAPs included in the U.S. EPA National Air Toxics Inventory (1999), ranked PAHs between 15 (Acenaphthene) to 29 (Dibenzo (a,h) anthracene) showing aircraft emission of 508.68 tons of 16-PAHs per year (compiled by USEPA, 2001), out which 0.41 tons of carcinogenic Benzo (a) pyrene, *B(a)P* was also emitted (URS Corporation for Federal Aviation Administration, Office of Environment and Energy, 2003).

A study characterizing aircraft turbine engine particulate emissions (Stockham et al; 1979) found the composition of the particles to be essentially carbon and to be less than 0.1micrometre in size. An earlier study at John F. Kennedy Airport found that 10% of the average total suspended particulate material (TSP) was organic in nature. Other particulate associated PAHs are also emitted from aircraft engines, representing a source of carcinogenic pollution (Clark et al, 1983).

In 1969, aviation was proven to be a potent source of carcinogenic polycyclic aromatic hydrocarbons (PAH). Extracts of soot from airplane engines produced cancer in practically 100% of the mice treated with such products (Shabad, 1980).

Soot collected from TU-104 engine contained 0.350 µg/g *B(a)P* and that from the IL-1 and AN-2 piston engines, 0.250 µg/g *B(a)P*, while the soot from

piston engine and turbo jet engine was found to have contained higher *B(a)P* concentration- 30 µg/g and 27 µg/g (Shabad, and Smirnov, 1972).

Aircraft engines eject considerable amounts of *B(a)P*, estimated (2-10 mg/minute). This causes an increase of *B(a)P* content (10 to 100-fold) in air, soil and airfield vegetation. Soil analysis revealed a *B(a)P* contamination level ranging from 0.012-0.068 µg/kg (Shabad, 1971).

These observations have been confirmed with data obtained at airfields of other towns particularly that in Riga, Latvia, USSR, where the airport was located within the city limits. In the residential area of Riga adjacent to the airfield, the *B(a)P* content of snow samples was 8 times higher than that at control site (Shabad, 1980).

### 2.3 PAHs in Soil

Most PAHs reach the soil via deposition from the atmosphere (Wilcke et al., 1996). It is estimated that more than 90% of the total burden of PAHs resides in the subsurface soils (Wu et al., 2005). Besides the deposition from the atmosphere, the type of land use also influences the PAH concentrations and patterns in soil. In soils, PAHs are generally immobile and persistent because of their low water solubility (Wilcke et al., 1996). Strong sorption coupled with very low water solubility and very low vapor pressures make leaching and volatilization insignificant pathway of PAHs dissipation (Skrbic et al., 2005). Thus soil is the part of the environment which accumulates most of the hydrophobic organic contaminants, such as PAHs (Maliszewska-Kordybach, 1996).

#### 2.3.1 Airport Soils

Soil was collected from a runway at one of Moscow airports showed *B(a)P* concentration between 0.0155-0.643 µg/g soil. Along the runway, *B(a)P* concentration was higher at the ends of the runway, rather than in the middle. The analysis of sweepings from the concrete covering of the runway showed a



content of *B(a)P* amounting to 0.182  $\mu\text{g/g}$ . Planes leaving or arriving at the airport move along strictly designated traffic lines or "corridors". The concentrations of *B(a)P* in samples taken from, the corridors of one of the Moscow airports, varied from 0.17 to 8.6  $\mu\text{g kg}^{-1}$  of soil, while the concentration at the control sites 1.5 km away from the airport showed a concentration less than 1.3  $\mu\text{g kg}^{-1}$ . The content of *B(a)P* in the soil samples collected under the traffic corridor of Pavlodar airport (Northern Kazakhstan) proved to be several times higher than the control site: up to 5.5  $\mu\text{g kg}^{-1}$ . Thus the comparison of the results of these studies leads to the conclusion that aviation exhausts do affect the *B(a)P* pollution of the environment (Shabad and Smirnov, 1972).

In Iceland, the soil of the landing field had up to 351  $\mu\text{g PAH/kg}$  with 2-3  $\mu\text{g}$  at the control site (Shabad, 1980).

The maximum concentration of total PAHs in surface soil samples at the South Tacoma airport, Washington, USA was detected to be 0.025  $\mu\text{g/g}$ , while the maximum probable carcinogenic PAH concentration was found to be 0.0126  $\mu\text{g/g}$  (ATSDR-PHA, South Tacoma Field, Washington, USA, 2006).

In the surface soil samples collected from a field near Nagoya Airport, Japan, the content of PAHs ranged from 0.034-0.278  $\mu\text{g/g}$  (Spitzer and Kuwatsuka, 1993).

It has been conjectured that jet turbine exhaust near airplane flight paths may result in significant human exposure to PAHs. U.S. EPA arranged access to a household located approximately 8 miles from the end of a runway at the Greater Cincinnati and Northern Kentucky Airport, U.S.A and collected soil, wipe and house dust samples in and around the household. The sums of the concentrations of probable human carcinogens (B2) and total target PAH,  $\Sigma_{19}\text{PAHs}$  in soil samples ranged from 0.036 to 0.42  $\mu\text{g/g}$ , and from 0.13 to 0.88  $\mu\text{g/g}$ , respectively. The concentrations of the well-known carcinogen,

Benzo(a)pyrene, *B(a)P* in the soil samples ranged from 0.001 to 0.53  $\mu\text{g/g}$ . With few exceptions, the sums of the concentrations of B2 PAH were approximately half of the total target PAH concentrations in these soil samples (Chuang, 1996).

Soil samples taken from a field inside the airport located in the East of France, characterized by an international traffic of 112000 planes per year, showed Benzo(b)fluoranthene and Fluoranthene as the major PAHs in airport soils. The  $\Sigma_{17}\text{PAH}$  concentration was found to be 0.325  $\mu\text{g/g}$  dry weights for the airport soil. 58% of the total concentration consisted of carcinogenic compounds. Benzo(a) pyrene was detected in the proportion (6%). The detected PAHs were mainly of high molecular weight. 86% of the total PAHs were detected to be 4 and more than 4 ring compounds. Higher levels of soil contamination were due to higher concentrations of more than 4 ring PAHs which are mainly in the particle phase and only deposited on leaves, easily washed off or windblown, or directly deposited on soil. PAH concentration in soil was due to the presence of high molecular weight compounds, and soil contamination occurred by deposition of PAHs from the aircraft emissions on to the surface soil. These PAHs also have a longer half-life and on the sampling sites they were under a continuous grass surface, protecting them from wind and photo-degradation (Ducoulombier and Rychen, 2003).

### 2.3.2 Rural Soils

The concentration of  $\Sigma_{11}\text{PAHs}$  collected from three rural areas of Estonia varied from 0.233 to 0.770  $\mu\text{g/g}$ . Typical soil PAH concentration derived from rural areas is estimated at about 0.10  $\mu\text{g/g}$  dry weights. The three dominant PAH found in the soil were Pyrene, Triphenylene and Fluoranthene in all areas under study (Trapido, 1999). The concentration range of 16 PAHs in rural soils (from the outskirts of Beijing, China) showed an average concentration of 0.016  $\mu\text{g/g}$  and a



median concentration of 0.0141 µg/g. The 4-6 ring PAHs represented about 66% in the rural samples (Ma et al., 2005).

### 2.3.3 Agricultural soils

Soil may be contaminated by the introduction of PAH containing products during agricultural operations. "Carbolineum", for instance, used as a herbicide, is a preparation based on shale tar and contains up to 7.0-9.0 µg/g *B(a)P*. The autumn samples showed higher *B(a)P* content in the top layer, apparently because of aerogenic soil contamination by agricultural machine exhausts. The *B(a)P* content in the samples from experimental fields was ten times that of the controls; not only in the top layer, but also in the subjacent layers, signifying a *B(a)P* penetration starting from the first days after application of the tar. The higher *B(a)P* content in the lower layer as compared to that of the middle one, may be due to the retention of *B(a)P* by the denser, unploughed soil. *B(a)P* content in air pollution is subject to seasonal changes; i.e. it is higher in winter than in summer, probably due to a higher rate of *B(a)P* decomposition by ultraviolet irradiation in summer (Shabad et al, 1971).

Weak contamination was observed in the agricultural soils in the Upper Silesia region of Poland. The  $\Sigma_{13}$ PAH concentration was detected to be 0.264 µg/g, while the average contents of individual hydrocarbons were below 0.030 µg/g (Maliszewska-Kordybach, 1996).

In north of Munich, in a typical rural region of Bavaria, Germany, the concentration of individual PAHs varied from 0.046 to 0.154 µg/g. The *B(a)P* level in soil varied from 2.4 to 11.4 µg/kg, which is in same range as those of arable soils of other regions in Germany-Sleswick- Holstein: 8 µg/kg *B(a)P*, North Rhine-Westphalia: 20 and 48 µg/kg *B(a)P*, Lower Saxony: 3-13 µg/kg *B(a)P* and 6 µg/kg (Martens et al., 1997) .

About one-third of the arable lands in Poland contain PAHs at the level  $<0.2 \mu\text{g/g}$  which is much below  $3.0 \mu\text{g/g}$  proposed in Germany as a precautionary value for PAHs in soils with humus content. The corresponding values for *B(a)P* were:  $0.028 \mu\text{g/g}$  and  $0.108 \mu\text{g/g}$  (Kordybach and Terelak, 1998).

PAH with three or more rings tend to be strongly adsorbed to the soil. The  $\Sigma_{16}\text{PAH}$  concentration in the agricultural soils of South Korea ranged from  $0.0233$  to  $2.834 \mu\text{g/g}$ . The mean concentration of total PAH for all samples collected was  $0.236 \mu\text{g/g}$  and the median concentration was  $0.158 \mu\text{g/g}$ . The general profile of PAH showed predominance of Fluoranthene (*Flan*), Benzo (b) fluoranthene (*B[b]F*) and Pyrene (*Pyr*) each containing 5, 5 and 4 rings respectively (Nam et al, 2003).

The agricultural soils of Tianjin, China from two sites showed  $\Sigma_{16}\text{PAH}$  concentrations of  $1.08$  and  $6.25 \mu\text{g/g}$  respectively. The dominant compounds in the soils were Naphthalene, Fluoranthene, and Chrysene for site A and Naphthalene, Phenanthrene and Fluoranthene for site B (Tao et al., 2004).

The vegetable soils of Guangzhou, China indicated that the concentration range of 16 PAHs was from  $0.042$  to  $3.077 \mu\text{g/g}$  and the pollution extent was classified as a "moderate level" in comparison to other investigations and soil quality standard. The contents of 3-ring PAHs, Acenaphthylene and Acenaphthene were very low. However, 5-ring PAHs, Phenanthrene, Chrysene and Benzo (b) fluoranthene dominate the overall 16 PAHs and their contents accounted for 64-78% of 16 PAHs in 0-20 cm surface soil samples (Chen et al., 2005).

#### **2.3.4 Soil around Railway tracks**

Soil samples collected from different areas of a railway junction from Ilawa Główna, Poland showed that PAH contamination of soil and plants was highest near the railway siding and lowest in the loading ramp and cleaning bay area. In

the railway siding soils, the  $\Sigma_{14}$ PAH concentration was found to be 2.178  $\mu\text{g/g}$ , while the individual PAH content varied from 0.0205 $\mu\text{g/g}$  to 0.367  $\mu\text{g/g}$ . Fluoranthene and Pyrene were detected as the dominant compounds. Carcinogenic PAHs, Benzo(a) pyrene, Indeno (1,2,3-cd) pyrene, Benzo (g,h,i) perylene, Dibenzo (a,h) anthracene were found in the order of concentrations 0.187, 0.172, 0.166 and 0.0205  $\mu\text{g/g}$  (Malawska and Wilkomirski, 2000).

### 2.3.5 Forest Soils

Along the North American Prairie, the  $\Sigma_{20}$ PAH concentration ranged from 0.063 to 0.321 $\mu\text{g/g}$ . Phenanthrene (38% of total  $\Sigma_{20}$ PAH concentration) and Naphthalene (28% of total  $\Sigma_{20}$ PAH concentration) were the most abundant PAHs. Soil organic carbon (SOC) concentrations correlated with the  $\Sigma_{20}$ PAH concentrations. The contribution of *Naph* to the  $\Sigma_{20}$ PAH decreased with increasing mean annual temperature (Wilcke and Amelung, 2000).

### 2.3.6 Suburban Soils

The concentration range of 16 PAHs was 3.884  $\mu\text{g/g}$  in suburban soils from the outskirts of Beijing, China with the relative standard deviation of 70.5% showed large differences in the extent of PAHs pollution at the various sampling sites. The median concentration of 8 carcinogenic PAHs in this study was 0.405  $\mu\text{g/g}$  in suburban soils (Ma et al., 2005).

### 2.3.7 River Bed Soils

10 PAHs were measured in the soils of 3 water-body bank in Hangzhou, China. It was observed that the sum of PAHs concentrations ranged from 0.0597 to 0.616  $\mu\text{g/g}$  dry weight in soils, with a mean concentration of 0.298  $\mu\text{g/g}$ . Three-ring PAHs dominated the soil and Fluorene showed maximum concentration (Chen, 2004).

### 2.3.8 Urban Roadway Soils

The PAH content of surface soils in the vicinity of heavy vehicular traffic near the Midlands motorway M6-A38 (M) in United Kingdom revealed that the top soil (0-4 cm) at a distance of 1m from the hard shoulder of the M6 motorway contained 20.0 µg/g of PAH comprising of Pyrene, Fluoranthene, Chrysene, Benz (a) anthracene, Benzo (a) pyrene, Benzo(e) pyrene and Coronene. At a distance of 600 m from the interchange the PAH concentration in surface soils (0-4 cm) were in the range 4.0-8.0 µg/g. These values were more than double the PAH concentrations found on the edge of the conurbation at Sutton Coldfield, UK (2.3 µg/g), while the site between Lichfield and Tanworth, U.K. showed only 0.026 µg/g of Pyrene and 0.016 µg/g of Fluoranthene in soil samples with trace amounts of other PAHs (Butler et al., 1984).

In a residential area located adjacent to the major arterial road (Kessels Road) in the district of Brisbane, Australia, concentration of  $\Sigma_{14}$ PAH was found to be 3.346 µg/g. The two most predominant PAHs in the soil samples were Benzo (g,h,i) perylene and Indeno (1,2,3-cd) pyrene ( 0.598 µg/g and 0.584 µg/g respectively) (Yang et al., 1991).

PAHs from vehicle exhausts and road runoff have been suggested as major sources of contamination of the roadside environment. Average  $\Sigma_{16}$ PAH concentration of 6 sampling sites of a roadside environment in Brisbane, Australia was found to be 0.471 µg/g wet wt. The carcinogenic PAHs, Benzo (a) anthracene, Chrysene, Benzo (a) pyrene, Benzo (e) pyrene, Benzo (k) fluoranthene and Indeno (1,2,3-c,d) pyrene comprised 57% of the total PAHs with Benzo (a) pyrene comprised 6% of the total. The Chrysene concentration had a good relationship to the total PAH concentration with a correlation coefficient of 0.99. Thus, the Chrysene content could be used to predict the general burden of PAHs in soil in the study area (Pathirana et al., 1994).

16 target PAHs were detected in all of the soil samples collected along the roadsides in the city of Chiang-Mai, Thailand. The mean concentration of 16 PAHs were found to be 0.824 µg/g. The geometric mean concentration of Pyrene was the highest, followed by Fluoranthene, Benzo (g,h,i) perylene and Coronene. The geometric mean concentration of *B(a)P* was 0.0202 µg/g soil (Amagai et al., 1999).

In soil samples collected from the eastern side slope of the A31 highway 30km north of Nancy, France the individual concentration of 16 EPA PAHs ranged from 0.003 to 41.811 µg/g. Low molecular weight PAHs such as Naphthalene, Fluorene, and Anthracene showed a concentration increase from 2 to 6 metre of the road, while high molecular weight PAHs such as Benzo (a) pyrene and Benzo (g,h,i) perylene show a concentration decrease from 2 to 6 metre of the highway (Bryselbout et al., 2000).

The concentration of 16 PAHs varied from 1.47 to 6.61 µg/g at a distance of 70 metre to 0.2 metre from the Jing-Chang highway, located in the north of Beijing, China. For most of the samples collected from a distance of 50 m to 0.2 m, the total concentration of 16 PAHs increased 3 to 5 times. The PAH concentration sharply decreased within first 10 metres, while substantial slower decrease continues beyond this distance (Chu et al., 2003).

The total PAH concentration in a pasture near a highway located in the north east of France ranged from 0.767µg/g dry weight (DW) to 3.989 µg/g DW, depending on the distance from the highway. The PAH distribution in soil decreased with distance from highway, from 2.627 µg/g DW to 1.228 µg/g DW. The major compounds found in the highway soil were Benz (f) fluoranthene and Fluoranthene, (concentration>0.160 µg/g DW), whose concentration represented more than 25% of the total PAH concentration (Crepineau et al., 2003).

### 2.3.9 Urban Soil

In the urban soil samples of Uberlandia, Brazil, the  $\Sigma_{20}$ PAH concentration ranged from 0.012 to 0.380  $\mu\text{g/g}$ . The most abundant compounds were Naphthalene (14% of the total), Benzo (b+j+k) fluoranthene (11% of the total), and Perylene (10% of the total). The most abundant PAHs in Uberlandia soils were *Naph > B(bjk)F > IP > B(ghi)P* (Wilcke et al., 1999).

The average of  $\Sigma_{16}$ PAHs was 0.611  $\mu\text{g/g}$  in urban soil samples of Tokushima, Japan. Anthracene was the main contaminant. The concentration of other PAHs was relatively low (Yang et al., 2002).

In the soil samples collected near chemical industries and unpolluted sites of Tarragona County (Catalonia, Spain), the  $\Sigma_{16}$ PAH concentration ranged between 0.112 and 1.002  $\mu\text{g/g}$  (dry weight) respectively. With the exception of Acenaphthylene, Acenaphthene, Anthracene and Benzo (k) fluoranthene, no significant differences in the levels of the remaining PAHs were found among the different zones of sample collection (Nadal et al., 2004).

The  $\Sigma_{16}$ PAH concentration in New Orleans, U. S. A, urban soils varied from 0.639 to 40.692  $\mu\text{g/g}$ . The average total PAH in urban soils was determined to be 5.562  $\mu\text{g/kg}$ , a level about 10 times higher than the background concentration in alluvium and rural soils. Of the 16 PAHs examined, the major compounds were Phenanthrene, Fluoranthene, Pyrene, Benzo (b) Fluoranthene and Benzo (a) pyrene (Wang et al., 2004)

The total content of 16 PAHs ranged from 0.307 to 1.452  $\mu\text{g/g}$  with arithmetic mean value of 0.667  $\mu\text{g/g}$  and a median of 0.382  $\mu\text{g/g}$ , represented typical PAH levels of urban soils throughout Novi Sad, Serbia. Considering the reported background PAHs concentrations in Bulgaria of 2-22  $\mu\text{g/kg}$  and suggested level of endogenous total PAHs concentration in soils of 1-10  $\mu\text{g/kg}$ , it could be concluded that the soils of Novi Sad were contaminated above the

natural and background level. But in accordance with the range of background PAHs levels of soil in Italy which were between 100-1000 µg/kg and upto 1000µg/kg in Czech Republic, the urban area of Novi Sad was not contaminated (Skrbic et al., 2005).

## **2.4 Preparation of sample for PAH analysis**

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

### **2.4.1 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 purification 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 no general 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).

#### **2.4.2 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 non aromatic, 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 a column, 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.

## **2.5 Analytical methods**

Hundreds of publications have described analytical methods for PAHs. 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 (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 analyze '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; the remaining compounds are commercially available as chemical standards with purities of 99% or higher.

### **2.5.1 Thin-layer chromatography**

Nowadays, thin-layer chromatography (TLC) is commonly limited to the identification of individual compounds (namely, B(a)P), 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), or in situ by scanning spectrofluorimetry (Borneff and Kunte, 1979).

### **2.5.2 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 analyze very complex mixtures containing over one hundred PAHs.

The most widely used stationary phases are the methylpolyisiloxanes: 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).

### **2.5.3 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 detectors 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).

#### **2.5.4 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*

### *Material and Methods*

**P**resent study was aimed to determine the levels of PAHs in the soils around the airport region. Indira Gandhi International (IGI) Airport, (South Delhi) was selected as the sampling site. Soil samples were collected from the periphery of the airport wherever it was accessible. In the IGI airport, runway is in the east to west direction. On the north, it is surrounded by Palam, a domestic airport so samples could not be collected from that side. A rural site, 5 km away from the airport having no emission source in the vicinity was chosen as background site. Sampling was done for a period of 6 months i.e. from November, 2005 to May, 2006 with the help of a stainless steel auger up to a depth of 5 cm.

### **3.1 Area of study**

#### **3.1.1 Delhi and its environment**

Delhi is situated at latitude of 28°24'17" to 28°53' and the longitude of 76°20'37" to 77°20'37" with an altitude of 216 metres 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 Gangetic plains lie in the east.

#### **3.1.2 Physiography**

The Union Territory of Delhi consists of flat and level plains interrupted a long continuous chain of rocky ridges. 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, and iii) the rocky outcrop of Aravalli called Kohi. The shape of the city can be said as circular with radial patterns.



### **3.1.3 Physiography of airport**

Indira Gandhi International (IGI) Airport located at 28° 33.41'N and 77° 05.21'E in the city of Delhi (Fig 3.1) covers an area of 64,000 square meters. It is 23 km south of New Delhi and is a vital link between India and rest of the globe. (<http://delhiairport.com>). It is one of the busiest airports in South Asia. Delhi operates 3 terminals: Terminal 1A and Terminal 1B at Palam Airport are domestic terminals and Terminal 2 at IGI Airport is an international terminal (<http://en.wikipedia.org/wiki/Delhi#Airports>). The International terminal (Terminal 2) is about 5 km away from the Domestic terminal (Terminal 1) at Palam ([www.worldairport.guide.co.uk](http://www.worldairport.guide.co.uk)). The International Terminal (Terminal 2) has 35 airlines flying to the major cities across the world and it has a terminal capacity of 1150 ([www.airportindia.org](http://www.airportindia.org)).

There are two runways at IGI airport: main runway 10-28 is made of paved surface in the direction of 10R/28L and has a length of 12,500 ft and an auxiliary runway 09-27 of paved surface, 9,229 ft in the direction 09L/27R. The main runway 10-28 is one of the few runways in Asia equipped with CAT III-B Instrument Landing System.

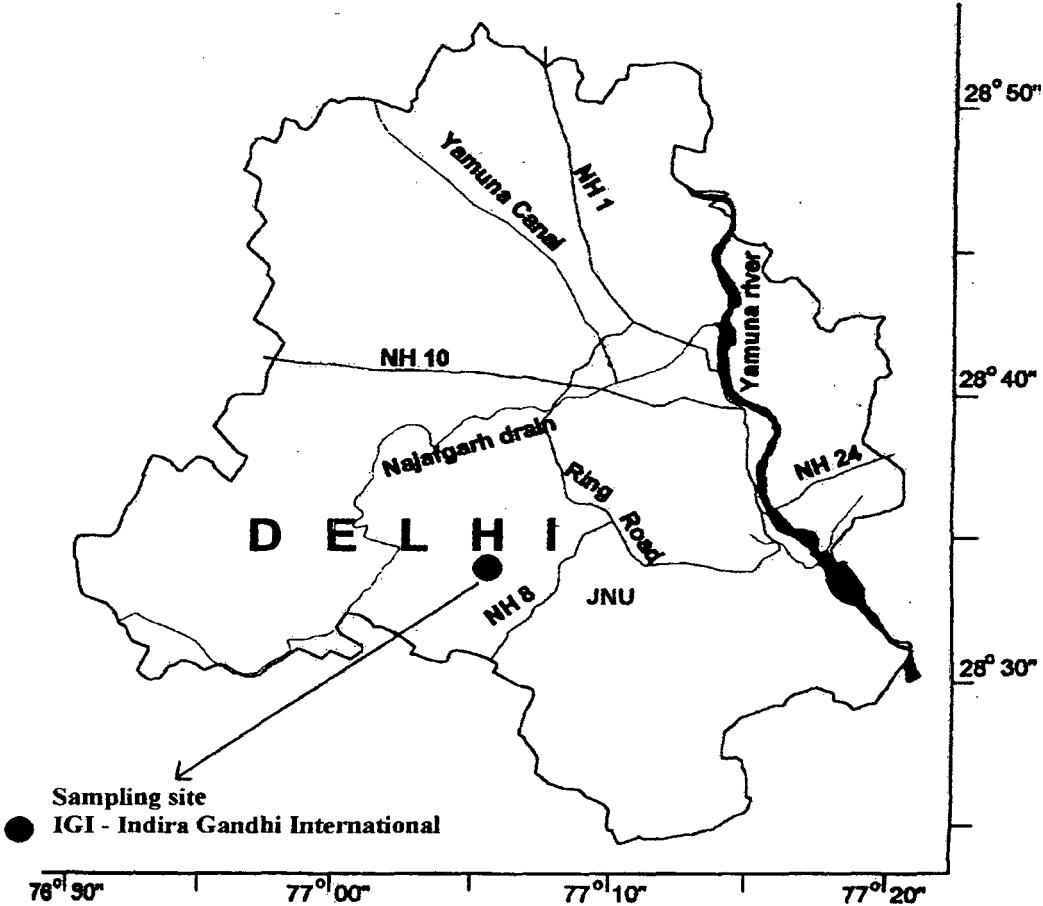
### **3.2 Sampling Sites**

The following sites were chosen around the IGI Airport.

#### **3.2.1 Site I: Terminal Park site (TP)**

This site was in a small park under the landing path of the airport terminal. The main pollution source at this site could be emission during landing operations of aircrafts. Vehicular emission from the nearby road traffic could be an additional source.

Fig 3.1 Map showing location of sampling site



### **3.2.2 Site II: Taxi/idle site (T/I)**

This site was in the south of the runway (east to west). Landing takes place from the east direction. There is an open land along this side and is about at 500-700 meters from the road. There are fuelling stations of Bharat Petroleum Corporation Limited (BPCL). The pollution sources at this site could be mainly aircraft emissions during taxiing in and out of the hangar and fuel emissions from the BPCL plant.

### **3.2.3 Site III: Take-off site (T-O)**

The sampling spot was taken in the backside of the IGI Airport i.e. in the west. Take-off of aircrafts occurs from this side. Shahbad Mohammadpur area is located in the vicinity. The Shahbad Railway station is situated about 10km from this site. A meter-gauge railway track runs parallel to the backside boundary of the airport. So, mainly aircrafts and railways can be accounted for the levels of PAHs at this site.

### **3.2.4 Site IV: Rural Site (R)**

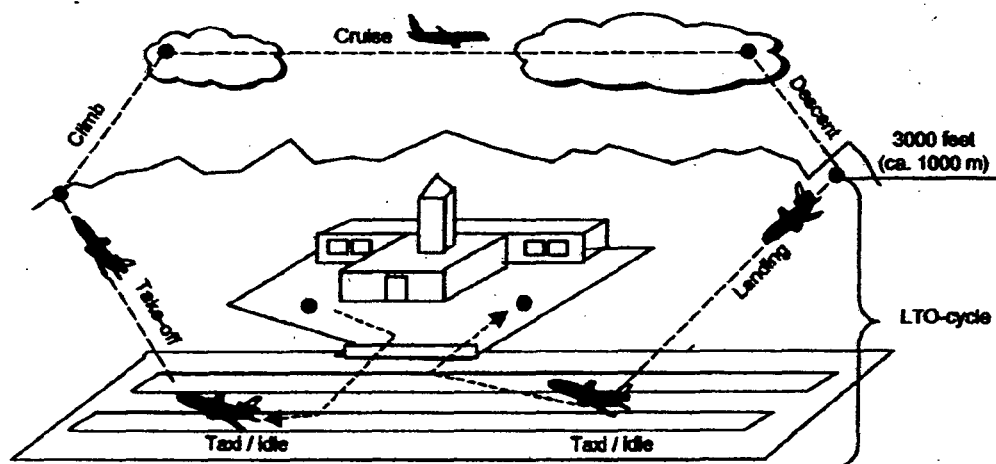
A rural site located 4-5 km away from the airport, having no known source of emission in the surroundings, i.e. no residential, industrial or vehicular emissions in the close vicinity. This sampling site was chosen as the background site, to compare the pollution in the airport vicinity with an unpolluted site.

### **3.3 Sample collection and preparation:**

The surface soils up to a depth of 1-5cm were collected by a metal core from the sampling sites. Samples were transferred into polythene bags and transported to the laboratory. Samples were taken from eight to ten spots at each site. In the lab, the samples were dried in the dark, twigs and stones were removed. Then the samples were homogenized and sieved to include particles of size range from 0-2 mm. After sieving the samples, they were mixed thoroughly

to make a composite sample. Quartering and coning was done to get the representative samples for further analysis.

Fig. 3.2 Standard flying cycle



### 3.4 Sample extraction and fractionation

Recent works 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, soil samples were extracted by ultrasonication, a method developed and verified by the various authors (Hong et al., 1995; Zhou et al., 2000). Soil samples (approximately 10-g dry weight) were extracted in 50 ml of toluene for 15 min by ultrasonic agitation (Misonix Ultrasonic Processor-XL) with a frequency of 20 KHz in a water bath (10-15°C). After 15 min the extract was taken out and then added freshly another 50 ml 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 eluant was discarded. Further elution was done by 20 ml of 1:1 hexane: toluene to obtain PAH fractions (Caricchia et al., 1999). The fraction containing PAHs were concentrated to 0.5-2ml by rotary evaporator. The sample was filtered by 0.20µm nylon filter and then transferred in a clean vial and stored at 4°C till further analysis.

### **3.5 HPLC analysis: Qualitative and Quantitative determination**

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 (20µL),

The PAH residue were separated by HPLC, and the individual PAHs were quantified using reference PAH standard (Supelco Inc. USA), and using Waters PAH C18 column. Gradient elution was executed with acetonitrile-water mixture. The PAH detection was made on a UV detector at wavelength 254 nm.

#### **3.5.1 Operating Condition**

Column: Waters PAH C18 (4.6 x 250 mm, 5µm-particle size)  
Temperature: 28°C ± 0.3°C

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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 detector- Detection at 254 nm
Injection volume:	20 $\mu$ l

The column was equilibrated for 30min before the first analysis. All the analyses were made in duplicates and their average is reported.

### 3.5.2 External standard calibration

External standard method was used for the calibration. It is one of the most common approaches to calibrations. It involves a simple comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards. Sample peak areas (or peak heights) are compared to peak areas (or heights) of the standards. The ratio of the detector response to the amount (mass) of analyte in the calibration standard is defined as the calibration factor (CF).

$$CF = \frac{\text{Peak area (or height) of the compound in the standard}}{\text{Mass of the compound injected (in nanograms)}}$$

Sixteen PAHs (16 compounds specified in EPA Method 610) in a mixture were obtained from Supelco (USA). Calibration standards of five concentration levels viz, 0.1 ppm, 0.5 ppm, 1ppm, 2 ppm and 3.0 ppm of external standard were prepared by diluting to 1000 $\mu$ l of volume with acetonitrile.

The working calibration curve and calibration factor 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 (USEPA, Method 8000B, 1996)

Concentration in the sample using the calibration factor was calculated by,

$$C (\mu\text{g/g}) = \frac{(As) (V_i)}{(V_t) (CF) (W_s) (1000)}$$

where,

As = Response for the parameter to be measured.

V<sub>t</sub> = Total volume of the concentrated extract (in μL).

CF = Calibration Factor (in nanogram<sup>-1</sup>)

W<sub>s</sub> = Amount of the sample extracted (gms).

V<sub>i</sub> = Volume of the extract injected (μL)

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

## *Chapter IV*

### *Results and Discussion*

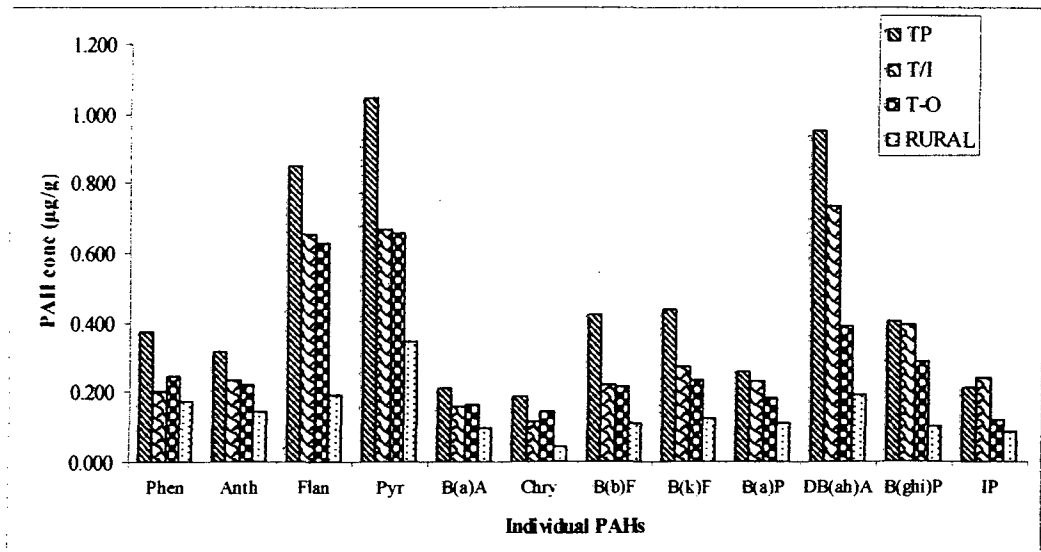


In the present study, PAHs concentrations were determined in the soils around an International airport (IGI) in Delhi. Soil samples were collected from 3 different locations viz: Terminal Park (TP), Taxi/Idle site (T/I) and Take-Off (T-O) surrounding the main airport area and a rural area (R) as a background site. In the soil samples, 12 different PAHs viz. 3-ring *Phen* and *Anth*, 4-ring *Flan*, *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 by HPLC and the results are tabulated in Table 4.1 to Table 4.4. Temporal and spatial variations (Fig. 4.2 and Fig. 4.1) were taken into consideration and compared with background concentrations from the rural site. Variation of Benzo [a] Pyrene, *B[a]P* (Fig. 4.9) has been discussed separately. Percentage distribution of individual PAHs (Fig. 4.3 - Fig. 4.7) and percentage distribution of different ring PAHs (Fig. 4.8) have been determined. PAH isomer pair ratios were used for source identification (Table 4.6- Table 4.8, Fig. 4.10).

#### **4.1 Spatial and Temporal variation of $\Sigma_{12}$ PAHs and relative distribution of individual PAHs at different sites**

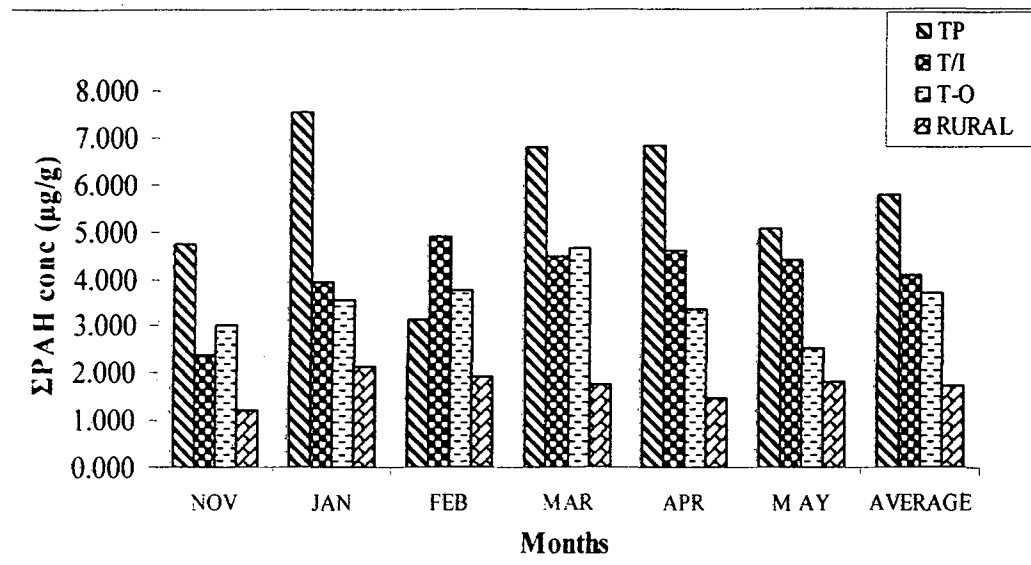
Total concentration of the 12 PAHs in the present study, is expressed as  $\Sigma_{12}$ PAH. In the airport site, it spanned from 2.394-7.529  $\mu\text{g/g}$  (Table 4.1-Table 4.4) with a mean of  $4.428 \pm 1.447$   $\mu\text{g/g}$ . Average  $\Sigma_{12}$ PAH concentration was found to be maximum ( $5.676 \pm 1.655$   $\mu\text{g/g}$ ) at Terminal Park (TP) site (Table 4.1), while it was minimum ( $3.487 \pm 0.726$   $\mu\text{g/g}$ ) at Take-Off site (T-O) (Table 4.3) of the airport. At other sites viz. Taxi/Idle site (T/I) and Rural site (R) average concentrations of  $4.122 \pm 0.901$   $\mu\text{g/g}$  (Table 4.2) and  $1.714 \pm 0.330$   $\mu\text{g/g}$  (Table 4.4) were recorded respectively. The concentration trends at different sites are discussed below.

Fig 4.1: Concentrations ( $\mu\text{g/g}$ ) of Individual PAHs at different sites in Delhi



On an average, among the three airport sites (TP, T/I and T-O), Terminal Park (TP) site showed the maximum PAH concentration (Table 4.1, Fig. 4.2), while Take-Off (T-O) site, showed minimum PAH concentration (Table 4.3, Fig. 4.2). No consistent temporal variation was observed at any site (Fig. 4.2).

Fig 4.2: Temporal variation ( $\mu\text{g/g}$ ) of  $\Sigma_{12}\text{PAH}$  at different sites



#### 4.1a) Site I: Terminal Park (TP)

At Terminal Park  $\Sigma_{12}$ PAH concentration varied from 3.131-7.529  $\mu\text{g/g}$  with a mean of  $5.676 \pm 1.655$   $\mu\text{g/g}$  (Table 4.1) for the study period. The observed maximum concentration of  $\Sigma_{12}$ PAH was in the month of January (Fig. 4.2). Temporal distribution did not reveal any consistent trend for  $\Sigma_{12}$ PAH concentration as well as individual PAHs. four-ring *Flan* and *Pyr*, and five-ring *DB[a,h]A* were the dominant compounds found at TP (Fig. 4.1).

**Table 4.1: PAHs concentrations ( $\mu\text{g/g}$ ) in the surface soils of Terminal Park (TP) site**

TP	Phen	Anth	Flan	Pyr	B(a)A	Chry	B(b)F	B(k)F	B(a)P	DB(ah)A	B(ghi)P	IP	SUM
NOV	0.423	0.233	0.685	0.761	0.200	0.178	0.306	0.649	0.234	0.449	0.438	0.182	4.738
JAN	0.518	0.378	1.006	1.234	0.272	0.200	0.590	1.008	0.328	1.263	0.307	0.427	7.529
FEB	0.099	0.238	0.638	0.685	0.135	0.109	0.213	0.214	0.166	0.271	0.234	0.131	3.131
MAR	0.244	0.356	1.031	1.232	0.315	0.183	0.377	0.281	0.070	1.962	0.562	0.155	6.767
APR	0.53	0.4	0.85	1.33	0.26	0.3	0.42	0.29	0.4	1.428	0.489	0.15	6.833
MAY	0.442	0.314	0.880	1.033	0.084	0.161	0.623	0.177	0.366	0.335	0.402	0.239	6.057
Average	0.376	0.319	0.848	1.045	0.212	0.188	0.421	0.437	0.260	0.951	0.405	0.213	5.676
SD	0.171	0.070	0.161	0.269	0.089	0.062	0.160	0.327	0.126	0.699	0.120	0.111	1.655

#### 4.1 b) Site II: Taxi/Idle (T/I) site

At the Taxi/Idle (T/I) site of IGI Airport,  $\Sigma_{12}$ PAH concentration ranged from 2.394–4.893  $\mu\text{g/g}$  with a mean of  $4.122 \pm 0.901$   $\mu\text{g/g}$  (Table 4.2). At this site maximum  $\Sigma_{12}$ PAH concentration was observed during the month of February (Fig. 4.2). The most abundant compounds detected at this were, four-ring *Pyr* and *Flan* and five-ring *DB[a,h]A* (Fig. 4.1).

**Table 4.2: PAHs concentrations ( $\mu\text{g/g}$ ) in the surface soils of Taxi/Idle (T/I) site**

T/I	Phen	Anth	Flan	Pyr	B(a)A	Chry	B(b)F	B(k)F	B(a)P	DB(ah)A	B(ghi)P	IP	SUM
NOV	0.077	0.203	0.333	0.329	0.086	0.062	0.173	0.234	0.146	0.378	0.272	0.101	2.394
JAN	0.156	0.351	0.583	0.631	0.068	0.140	0.121	0.201	0.331	0.955	0.263	0.150	3.949
FEB	0.332	0.258	0.774	0.738	0.191	0.128	0.273	0.309	0.253	0.594	0.643	0.401	4.893
MAR	0.173	0.148	0.935	0.883	0.240	0.126	0.219	0.344	0.309	0.424	0.440	0.260	4.502
APR	0.319	0.172	0.862	0.686	0.203	0.132	0.245	0.372	0.249	0.667	0.311	0.397	4.614
MAY	0.138	0.278	0.436	0.738	0.149	0.115	0.305	0.191	0.084	1.385	0.433	0.125	4.377
Average	0.199	0.235	0.654	0.668	0.156	0.117	0.223	0.275	0.229	0.734	0.394	0.239	4.122
SD	0.103	0.075	0.242	0.186	0.068	0.028	0.067	0.077	0.095	0.379	0.145	0.135	0.901

#### 4.1 c) Site III: Take-off (T-O) site

At the take-off site of IGI Airport,  $\Sigma_{12}$ PAH concentration ranged from 2.517- 4.661  $\mu\text{g/g}$  with a mean of  $3.487 \pm 0.726$   $\mu\text{g/g}$  (Table 4.3).  $\Sigma_{12}$ PAH concentration at this site was maximum for the month of February (Fig. 4.2). The dominant compounds at this sampling site were four-ring *Pyr*, *Flan* and five-ring *DB[a,h]A* (Fig. 4.1).

**Table 4.3: PAHs concentrations ( $\mu\text{g/g}$ ) in the surface soils of Take-Off (T-O) site**

T-O	Phen	Anth	Flan	Pyr	B(a)A	Chry	B(b)F	B(k)F	B(a)P	DB(ah)A	B(ghi)P	IP	SUM
NOV	0.281	0.088	0.727	0.710	0.153	0.134	0.192	0.162	0.146	0.187	0.174	0.074	3.029
JAN	0.267	0.320	0.674	0.627	0.177	0.120	0.191	0.462	0.069	0.319	0.212	0.137	3.574
FEB	0.148	0.317	0.794	0.813	0.184	0.116	0.224	0.255	0.177	0.411	0.265	0.069	3.773
MAR	0.390	0.273	0.822	0.785	0.203	0.128	0.228	0.308	0.250	0.567	0.460	0.246	4.661
APR	0.300	0.129	0.364	0.638	0.174	0.291	0.118	0.097	0.228	0.599	0.362	0.070	3.370
MAY	0.078	0.202	0.393	0.359	0.089	0.065	0.332	0.136	0.220	0.257	0.265	0.121	2.517
Average	0.244	0.221	0.629	0.655	0.163	0.142	0.214	0.237	0.182	0.390	0.290	0.119	3.487
SD	0.113	0.098	0.201	0.163	0.040	0.077	0.070	0.135	0.067	0.167	0.105	0.068	0.726

#### 4.1 d) Site IV: Rural (R) site

At the rural site (R), the average  $\Sigma_{12}$ PAH concentration was  $1.714 \pm 0.330$   $\mu\text{g/g}$  shown in (Table 4.4). The dominant PAHs present in the site were three ring *Phen* and *Anth*, four ring *Flan* and *Pyr* and five ring *DB[a,h]A* (Fig. 4.1).

**Table 4.4: PAHs concentrations ( $\mu\text{g/g}$ ) in the surface soils of Rural (R) site in Delhi**

RURAL	Phen	Anth	Flan	Pyr	B(a)A	Chry	B(b)F	B(k)F	B(a)P	DB(ah)A	B(ghi)P	IP	SUM
NOV	0.097	0.171	0.077	0.398	0.081	0.018	0.079	0.086	0.073	0.029	0.086	0.010	1.205
JAN	0.248	0.145	0.324	0.405	0.105	0.058	0.105	0.141	0.122	0.250	0.122	0.102	2.127
FEB	0.195	0.156	0.227	0.391	0.112	0.041	0.116	0.129	0.134	0.210	0.098	0.121	1.930
MAR	0.18	0.13	0.2	0.3	0.1	0.05	0.12	0.13	0.12	0.224	0.111	0.1	1.757
APR	0.13	0.13	0.12	0.27	0.09	0.03	0.11	0.12	0.1	0.198	0.085	0.09	1.469
MAY	0.18	0.13	0.21	0.31	0.09	0.06	0.13	0.13	0.12	0.236	0.101	0.09	1.793
Average	0.172	0.144	0.194	0.345	0.095	0.044	0.110	0.123	0.112	0.191	0.100	0.084	1.714
SD	0.052	0.017	0.087	0.059	0.012	0.017	0.017	0.019	0.022	0.082	0.014	0.038	0.330

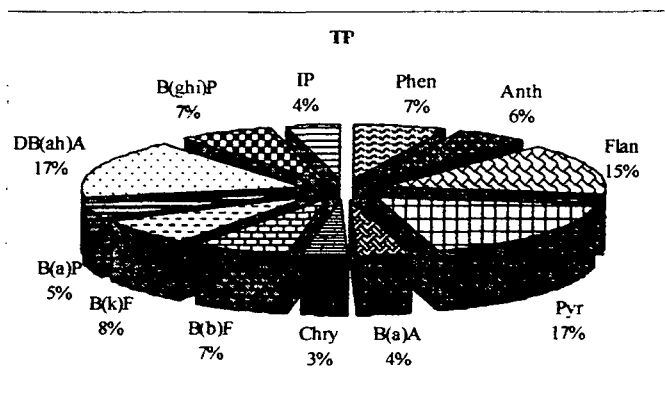
#### 4.2 Percentage Distribution

Percentage distribution of average concentrations of individual PAHs at all the four sampling sites are given in the Fig.4.3-Fig.4.6 and the average percentage distribution of individual PAHs (of all the airport sites) is given in Fig.4.7.

##### 4.2 a) Site I: Terminal Park (TP)

Percentage distribution at TP showed that *Pyr* and *DB[a,h]A* (17%) were the most abundant compounds (Fig. 4.3), followed by *Flan* (15%)> *B[k]F*(8%)> *B[b]F*, *B[g,h,i]P* and *Phen* (7%)> *Anth* (6%)> *B[a]P* (5%)> *B[a]A* and *IP*(4%)> *Chry* (3%).

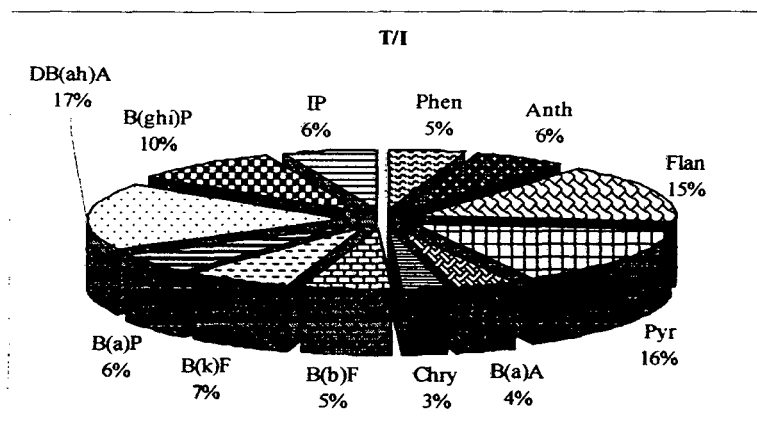
Fig. 4.3: Percentage distribution of individual PAHs at TP site



##### 4.2 b) Site II: Taxi/Idle (T/I) site

At T/I site, the major compound present was *DB[a,h]A* (17%) (Fig. 4.4), followed by *Pyr* (16%)> *Flan* (15%)> *B[g,h,i]P* (10%)> *B[k]F* (7%)> *Anth*, *B[a]P* and *IP* (6%)> *Phen* and *B[b]F* (5%)> *B[a]A* (4%)> *Chry* (3%).

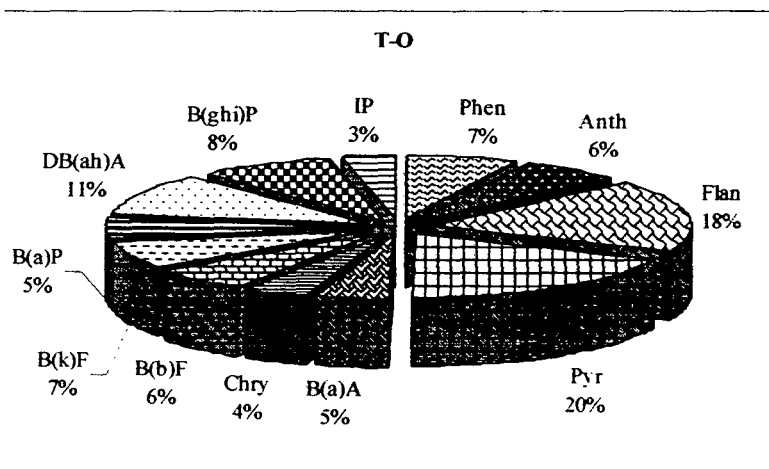
Fig. 4.4: Percentage distribution of individual PAHs at T/I site



#### 4.2 c) Site III: Take-off (T-O) site

At T-O, the dominant compound was *Pyr* (20%) (Fig. 4.5), followed by *Flan* (18%) > *DB[a,h]A* (11%) > *B[g,h,i]P* (8%) > *B[k]F* and *Phen* (7%) > *B[b]F* and *Anth* (6%) > *B[a]P* and *B[a]A* (5%) > *Chry* (4%) > *IP* (3%).

Fig. 4.5: Percentage distribution of individual PAHs at T-O site





4.2 d) Site IV: Rural site (R)

At the rural site (R), the major compound present was *Pyr* (20%) (Fig. 4.6), followed by *Flan* and *DB[a,h]A* (11%) > *Phen* (10%) > *Anth* (8%) > *B[a]P* and *B[k]F* (7%) > *B[a]A*, *B[b]F*, and *B[g,h,i]P* (6%) > *IP* (5%) > *Chry* (3%).

Fig. 4.6: Percentage distribution of individual PAHs at Rural site

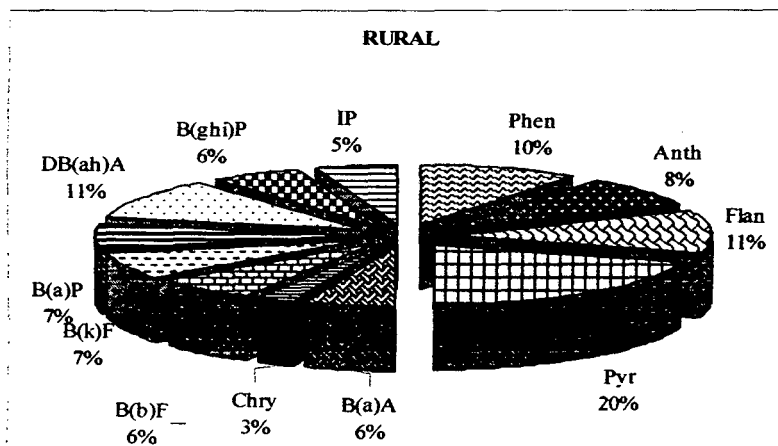
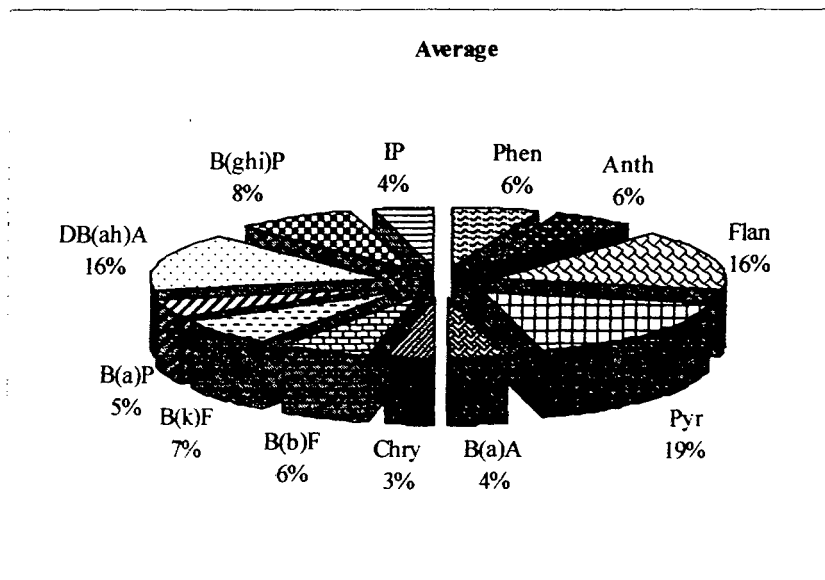


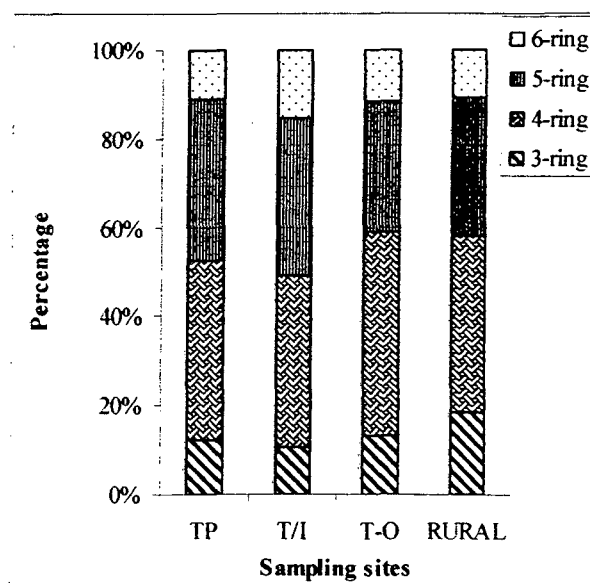
Fig 4.7: Average (of all sites around the airport) percentage distribution of individual PAHs



Among the 12 PAHs, 4-ring *Pyr* was the most abundant compound at all the sites with an average of 19% for the airport region (Fig. 4.7), and 20% at rural site (Fig. 4.6). *Chry* was the least abundant compound (Fig. 4.6 and Fig. 4.7) at all the locations (average of 3%).

Another abundant 4-ring compound was *Flan* with an average of 16% for the airport region (Fig. 4.7), and 11% for rural site (Fig. 4.6). Among 5-ring PAHs, *DB[a,h]A* showed high percentage at all the sites, 16% in the airport site (Fig. 4.7), and 11% in the rural site (Fig. 4.6). At the rural site (Fig. 4.6), 3-ring PAHs *Phen* (10%) and *Anth* (8%) were also present in significant proportions. Thus, showing the presence of low molecular weight PAHs at this site.

**Fig. 4.8: Percentage composition of 3-, 4-, 5- and 6-ring PAHs in the Soils of different sites (3-ring PAHs include *Phen* and *Anth*; 4-ring PAHs include *Flan*, *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 *B[ghi]P* and *IP*)**



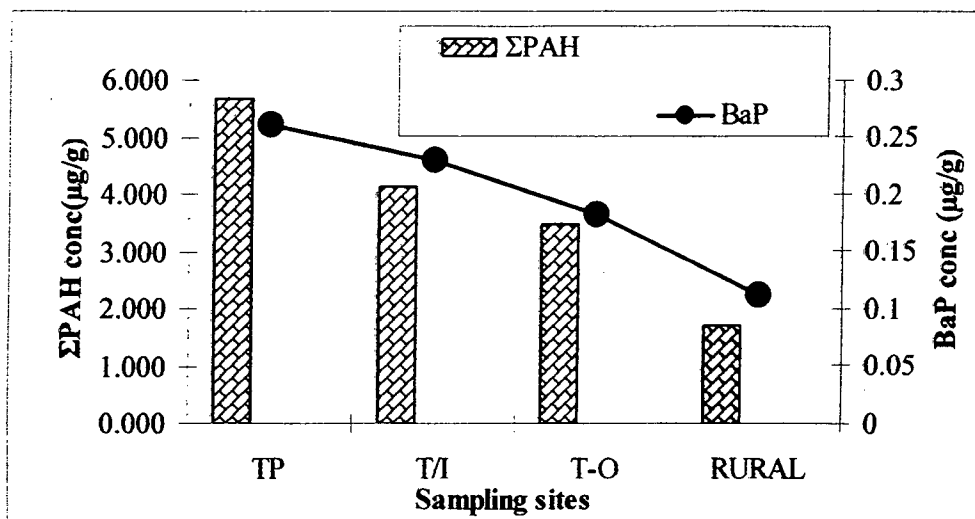
4- and 5-ring compounds together accounted for more than 70% of  $\Sigma_{12}$ PAHs at all the sites (Fig. 4.8). At all the sites 4 & 5-ring PAHs were found to be dominant (Fig. 4.8). Similar findings were reported by Ducoulombier and Rychen (2003), showing that 4 and >4 ring PAHs dominated the soils around an airport located at the East of France, and formed 86% of the total PAHs. PAHs with 4 or more aromatic rings are persistent in the environment (Mackay et al., 1992) PAHs with three or more rings tend to be strongly adsorbed onto the soils. Strong sorption, leaching coupled with very low water solubility and very low pressures make leaching and volatilization insignificant pathway of PAH dissipation (Park et al., 1990).

#### 4.3 Variation in B(a)P concentrations:

Benzo [a] Pyrene, *B(a)P* is a well known carcinogenic hydrocarbon and the best known model compound of the group of polycyclic hydrocarbons. Aviation seems to be a significant source of environmental contamination by carcinogenic hydrocarbons.

Aircraft engines emit considerable amounts of *B(a)P*, estimated to be 2-10 mg per minute. Soot collected from TU-104 engine contained 0.35 $\mu$ g/g *B(a)P* and that from the IL-1 and AN-2 piston engines, 0.25 $\mu$ g/g *B(a)P*, while the soot from piston engine and turbo-jet engine was found to have contained higher *B(a)P* concentration- 30 $\mu$ g/g and 27 $\mu$ g/g respectively. This causes an increase in *B(a)P* content (10-100 fold) in air, soil and airfield vegetation (Shabad, 1971).

In the present study, the variation in *B(a)P* with  $\Sigma_{12}$ PAH is shown in (Fig. 4.9). At all the sites, the *B(a)P* concentration varied linearly with  $\Sigma_{12}$ PAH concentration. The *B(a)P* concentration ranged from 0.069 to 0.395  $\mu$ g/g (Table 4.1-4.4) with a mean of 0.233 $\pm$ 0.099  $\mu$ g/g for the airport site. The percentage of *B(a)P* did not show much variation for the airport with an average value of 5% (Fig. 4.7), while

Fig 4.9: Variation of B[a]P and  $\Sigma_{12}$ PAH at different sites

the rural site showed 7% of *B(a)P* concentration (Fig. 4.6).

The *B(a)P* concentration around IGI Airport in Delhi ( $0.233 \pm 0.099 \mu\text{g/g}$ ) was found to be much higher as compared to the *B(a)P* concentration in the French airport soils ( $0.026 \mu\text{g/g}$ ) (Ducoulombier and Rychen, 2003), but the 5% *B(a)P* concentration around IGI airport soil (Fig. 4.7) was comparable to 6% *B(a)P* at French airport soil. IGI airport soil *B(a)P* concentration was far greater than in the soil around the runway of Moscow Airport (ranged from  $0.016$  to  $0.064 \mu\text{g/g}$ ) (Shabad and Smimov, 1971). The *B(a)P* content in soil samples collected under the traffic corridors of Pavlodar Airport (Northern Kazakhstan) showed much lesser concentration of  $0.006 \mu\text{g/g}$ . (Shabad and Smimov, 1971). Analysis of soil collected from household near the Greater Cincinnati and Northern Kentucky airport showed comparable *B(a)P* concentration varying from  $0.001$ - $0.53 \mu\text{g/g}$  (Chuang, 1996). Comparable *B(a)P* concentration was also reported at

Nagoya Airport, Japan (0.225 µg/g), providing an evidence of *B(a)P* from aircraft turbine particulate emissions (Spitzer and Kuwatsuka, 1993).

#### 4.4 Discussion

The analysis of PAHs in surface soils around IGI Airport showed that  $\Sigma_{12}$ PAH concentrations were heterogeneously distributed at different sites throughout the airport. Differences were observed among the various sites of the airport (Fig. 4.9). The processes controlling the level of PAHs in soil are complex. Among important factors are chemical properties of the compounds, the composition of the soil such as organic carbon and clay content, and soil patterns. Many chemical and physical factors such as aviation fuel composition, emissions during landing and take-off (LTO cycles) of aircraft, combustion temperature of the aircraft engine during PAH formation, age of the aircraft, transport mechanisms, wind direction, other meteorological factors and sampling scheme might have influenced the concentration of PAHs around the airport.

Nevertheless, the concentration measured in this study represents steady-state equilibrium at that point in time that resulted from the interactions of all 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 viz. runway and adjoining airport enclosure region.

Variation in the concentration of  $\Sigma_{12}$ PAH around the IGI Airport, and rural site is depicted in Fig. 4.9. The  $\Sigma_{12}$ PAH concentrations increased gradually from the Take-off side (T-O) of the airport to the Terminal park (TP) and attained a maximum value at TP (Fig. 4.9). Hence, PAH level was minimum in the soils of Take-off (T-O) side while it was comparatively higher at Taxi/idle side (T/I) and finally reached maximum at Terminal Park (TP).

This finding is in agreement with the studies showing that PAH emissions are dependent on the power setting of the aircraft engine. Hydrocarbon emission from aircrafts, result from incomplete combustion at lower power setting used for

descent or when idling or taxiing on the ground ([www. average-aerospace.com/html/environment.html](http://www.average-aerospace.com/html/environment.html)) and tend to decrease as power setting increases i.e. during take-off (Ambient Air Pollution, 2001). As landing at the IGI Airport, occurs from the east-west direction and Terminal Park is located close to the runway, under the landing park, high emission of PAHs during landing might have contributed to the high PAH values at TP. Moreover, as this site is close to the airport terminal so vehicular traffic might have also augmented the PAH concentration at this site.

The following table (Table 4.5) shows the typical emission index (g/kg) levels showing that emission of hydrocarbon is maximum during idling or descent and minimum during take-off by 8 times ([www.grida.no/climate/ipcc/aviation](http://www.grida.no/climate/ipcc/aviation)). Thus, PAH emissions are minimum during take-off and maximum during landing ([www.grida.no/climate/ipcc/aviation](http://www.grida.no/climate/ipcc/aviation)).

**Table 4.5: Typical emission index (g/kg) levels for engine operating regimes**

Species	Idle	Take-off	Cruise
Hydrocarbon	4 (0-12)	0.5	0.2-1.3

Around the IGI Airport, the major PAHs found were *Pyr*, *Flan*, *DB(a,h)A*, with average concentrations of 0.63, 0.55 and 0.52 $\mu$ g/g respectively (Fig. 4.1). Similar dominant compounds e.g. *Flan* and *Pyr* were reported in the French airport soil (Ducoulombier and Rychen, 2003).

In all the sites, the dominant compounds were *Pyr*, *Flan*, *DB[a,h]A* (Fig. 4.1), suggesting a common emission source. According to literature, *Flan* 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). *Flan* is considered as a good

pollution indicator in environments impacted by urban and industrial activities (Chaudhry, 1994). A dominance of *Pyr* over *Flan* is also clear from Fig.4.1. During the combustion process, *Pyr* is more stable than *Flan* and hence they are characteristic pyrolytic products. *Phen*, *Flan*, *Pyr*, *IP* and *B(ghi)P* are also considered to be vehicle markers of PAHs and they support the vehicle origin as the main cause of diffusion of PAHs in the studied site (Garcia-Alonso et al., 2003).

*DB[ah]A*, another dominant compound at all sites (11-16%) (Fig. 4.6 and Fig. 4.7), 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>). *DB[a,h]A* is also found to be present in emissions from coal combustion and oil stoves, but not vehicular exhaust (Yang et al., 1991). This justifies the high concentration of *DB[a,h]A* at the airport and background sites.

*B[b]F* varies from 5-7% (Fig. 4.6 and Fig. 4.7) in the present study. It 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* (occurring 7-8%) (Fig. 4.6 and Fig. 4.7) 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 (<http://www.anr.state.vt.us>).

*Chry* concentration was observed to be minimum (average of 3%) at all the sites (Fig. 4.6 and Fig. 4.7). *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 minor contribution to the total PAH concentration also indicates low

emissions from coal combustion and emission from calcination of biological samples close to the sampling site (Garcia-Alonso et al., 2003) and natural sources.

The average  $\sum_{12}$ PAH concentration in the IGI Airport soil ( $4.428 \pm 1.447 \mu\text{g/g}$ ) was much higher as compared to other airport soil studies. The  $\sum_{16}$ PAH concentration reported in the French airport soil was  $0.322 \mu\text{g/g}$  (Ducoulombier and Rychen, 2003). Soil collected from household near the Greater Cincinnati and Northern Kentucky airport showed  $\sum_{19}$ PAH concentration varying from  $0.13$ - $0.88 \mu\text{g/g}$  (Chuang, 1996). PAH concentration upto  $0.351 \mu\text{g/g}$  was detected in the soil of a landing field of Iceland (Shabad, 1980). Maximum concentration of total PAHs in surface soil samples at the South Tacoma airport was detected to be  $0.025 \mu\text{g/g}$ , while the maximum probable carcinogenic PAH concentration was found to be  $0.0126 \mu\text{g/g}$  (ATSDR-PHA, South Tacoma Field, U. S. A).

The hydrocarbon emission from aircrafts is also dependent on the average age of the aircrafts. It has been observed that with newer aircrafts, the hydrocarbon emission decreases by 10% (GAO Report, 2003). The Indian Government imports aircrafts having an average age of 15 years (Business line, July 10, 2004), while the commercial Indian fleet has an average age of 22.8 years. ([www.blonnet.com](http://www.blonnet.com)). So we can say that the high PAH emission at the IGI Airport may be due to the usage of old aircraft models.

Thus it can be concluded, that the dominant origin of PAHs in the soils around the IGI Airport had a pyrogenic fingerprint that resulted from the incomplete combustion of aviation fuel during landing process of aircrafts.

Vehicular emission is a common source of pollution in the urban environment, and also at the sampling sites. As the airport is not in the proximity of any industrial area, so emission from industries can be ruled out. Hence the



alternate emission source in the airport soils could be due to the emission from allied activities taking place at the airport.

The rural (R) site, having no source of emission in the vicinity, showed an average  $\Sigma_{12}$ PAH concentration of  $1.714 \pm 0.330 \mu\text{g/g}$  (Table 4.4). The major compounds observed at R were *Pyr*, *Flan*, *DB[a,h]A* and *Phen* with average concentrations of 0.345, 0.194, 0.191 and  $0.172 \mu\text{g/g}$  respectively (Fig. 4.6 and Table 4.4).

Thus, the total PAH concentration around IGI Airport is higher by 2.58 times than at the rural site. Similar type of studies were performed in USSR in order to determine whether aviation exhausts induce local *B(a)P* pollution. Soil samples collected from the Moscow airport showed *B(a)P* concentration between  $15.5\text{--}64.3 \mu\text{g/kg}$ , while 32 control soil samples taken within the 20km radius around the Moscow airport showed a much lesser *B(a)P* pollution of 1.17 to  $8.6 \mu\text{g/kg}$  (Shabad and Smimov, 1976).

These observations have been confirmed with data obtained at airfields of other towns, particularly that in Riga, Latvia, USSR, where the airport is located within the city limits. In the residential area of Riga adjacent to the airfield, the *B(a)P* content of snow samples was 8-9 times higher than that in samples from other parts of the city (Shabad, 1980).

Soil samples were taken within a 20km radius of Pavlodar airport (Northern Kazakhstan), where industry and traffic was much less prevalent than in the suburbs of Moscow. It showed up to  $5.5 \mu\text{g kg}^{-1}$  *B(a)P* content taken under the "corridors" near Pavlodar airport, several times greater than the background pollution observed in the control site (less than  $1 \mu\text{g kg}^{-1}$ ). Thus the comparison of the results of these studies leads to the conclusion that aviation exhausts do affect the *B(a)P* pollution of the environment (Shabad and Smimov, 1972).

Since *B(a)P* is very persistent in the environment, the pollution of the soil reflects the total pollution in the district, summed up for at least a few years, perhaps even decades (Shabad and Smirnov, 1972).

In 1996, it has been conjectured that jet turbine exhaust near airplane flight paths may result in significant human exposure to PAHs. U.S. EPA arranged access to a household located approximately 8 miles from the end of the of a runway at the Greater Cincinnati and Northern Kentucky Airport, and collected soil, wipe and house dust samples in and around the household. The sums of the concentrations of probable human carcinogens (B2) and total target PAH,  $\Sigma_{19}$ PAHs in soil samples ranged from 0.036 to 0.42  $\mu\text{g/g}$ , and from 0.13 to 0.88  $\mu\text{g/g}$ , respectively (Chuang, 1996).

Thus this proves that the aviation exhausts do pollute the local environment. Hence airports should be located away from the city limits in order to prevent a large population residing in the airport adjoining areas from exposure to carcinogenic compounds.

#### 4.5 Source apportionment

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, the following four PAH isomer pair ratios were applied as distinct tracers to identify possible sources of PAH in soil samples: Anthracene/Anthracene + Phenanthrene (*Anth*/178); Benzo[a]Anthracene/Benzo[a]Anthracene + Chrysene (*BaA*/228); Fluoranthene/Fluoranthene + Pyrene (*F/F* + *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 soil 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). Additionally, for each soil sample PAH isomer pair ratios, *Anth/178*, *BaA/228* and  $IP/IP + B[ghi]P$  were plotted against  $F/Fl + Pyr$  to show how PAH distribute relative to their possible sources (Fig. 4.10, 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;  $F/Fl + Pyr$  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 airport soils are derived primarily from combustion sources (Fig. 4.10 and Table 4.6- Table 4.10). Possible major sources of combustion derived PAH include fossil fuels/petroleum (kerosene, 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 soils 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 (Table 4.6 and Table 4.7) ranged from 0.355-0.707 at TP with a mean of 0.487, 0.351-0.726 with a mean of 0.556 at T/I, 0.238-0.722 with a mean of 0.483 at T-O and from 0.368-0.639 with a mean of 0.465 at rural site (Fig. 4.10). Average for all the sites was found to be >0.10 indicating dominance of combustion as the major source of PAHs.

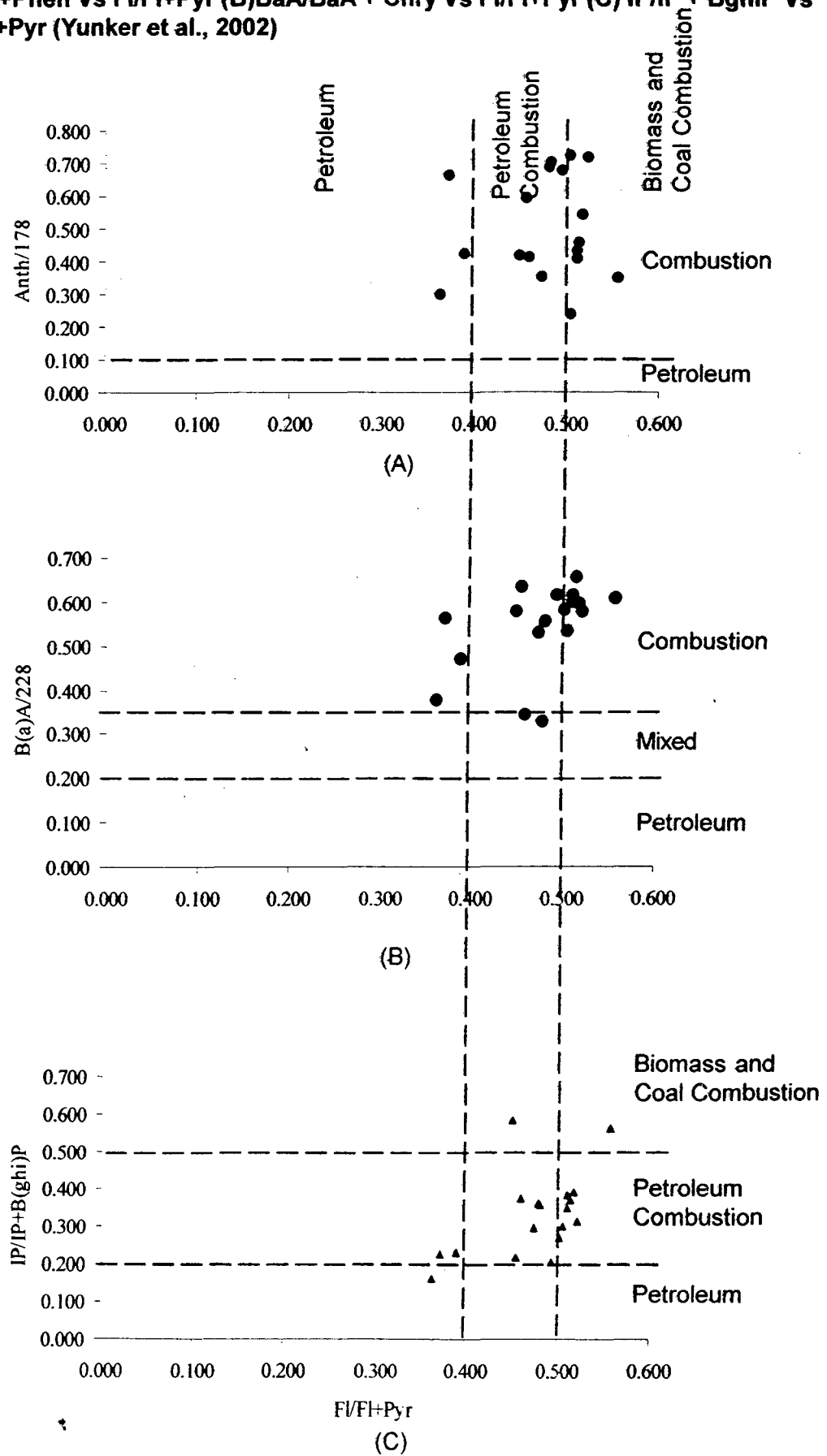
Table 4.6: PAH isomer pair ratios at different sites

	TP				T/I				T-O			
	Anth/178	B(a)A/228	Fl/Fl+Pyr	IP/IP+B(ghi)P	Anth/178	B(a)A/228	Fl/Fl+Pyr	IP/IP+B(ghi)P	Anth/178	B(a)A/228	Fl/Fl+Pyr	IP/IP+B(ghi)P
NOV	0.355	0.53	0.474	0.294	0.726	0.582	0.503	0.271	0.238	0.533	0.506	0.298
JAN	0.421	0.577	0.449	0.582	0.692	0.327	0.48	0.363	0.545	0.596	0.518	0.393
FEB	0.707	0.554	0.482	0.358	0.437	0.598	0.512	0.384	0.682	0.614	0.494	0.206
MAR	0.593	0.633	0.456	0.216	0.461	0.656	0.514	0.371	0.412	0.614	0.512	0.349
APR	0.427	0.47	0.389	0.231	0.351	0.605	0.557	0.561	0.3	0.374	0.363	0.162
MAY	0.415	0.343	0.46	0.373	0.667	0.563	0.371	0.225	0.722	0.577	0.522	0.313
Average	0.487	0.518	0.452	0.342	0.556	0.555	0.489	0.362	0.483	0.551	0.486	0.287
SD	0.134	0.101	0.033	0.134	0.158	0.116	0.063	0.116	0.199	0.092	0.061	0.087

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RURAL	Anth/178	B(a)A/228	Fl/Fl+Pyr	IP/IP+B(ghi)P
NOV	0.639	0.821	0.162	0.102
JAN	0.368	0.644	0.445	0.456
FEB	0.444	0.732	0.367	0.553
MAR	0.431	0.653	0.402	0.466
APR	0.49	0.731	0.308	0.503
MAY	0.415	0.583	0.408	0.468
Average	0.465	0.694	0.349	0.425
SD	0.094	0.084	0.102	0.162

**Fig 4.10: Plots of PAHs isomers pair ratios for source identification: (A) Anth/Anth+Phen Vs Fl/Fl+Pyr (B) BaA/BaA + Chry Vs Fl/Fl+Pyr (C) IP/IP + BghiP Vs Fl/Fl+Pyr (Yunker et al., 2002)**



in the soils are derived primarily from combustion of diesel and wood (at all airport sites), bituminous coal (at TP), and coal tar (at T/I and T-O) (Fig. 4.10) with minor occurrences of PAH from mixed (combustion and petroleum) sources. Unburnt fossil fuel, specifically diesel oil (at all sites), and asphalt (at TP) are minor contributors of PAH at all the stations. The *B[a]A/228* isomer ratios for the samples closely match those determined from environmental samples that include used engine oil, gasoline passenger car (at TP), tunnel with light-duty gasoline vehicles (TP), tunnel with heavy-duty diesel trucks and gasoline vehicles (all sites except at TP and R) and creosote treated wood piling (at TP). At R, the only possible source of emission was found to be unburnt diesel oil.

*Fl/202* isomer pair ratio (Table 4.6 and Table 4.7) ranged from 0.389-0.482 at TP with a mean of 0.452, 0.371-0.557 with a mean of 0.489 at T/I, 0.363-0.522 with a mean of 0.486 at T-O and from 0.162-0.445 with a mean of 0.349 at rural site. The *F1/F1 + Pyr* isomer pair ratios (Table 4.9) show that in the surface soils of IGI Airport, combustion of wood (at all sites except R), gasoline (at TP), diesel (at all sites) and fuel oil (at T/I and T-O) and bituminous coal (all sites except TP and R) are the possible major sources of PAH. Unburnt petroleum, specifically diesel oil (at all sites), lubricating oil (at R) and kerosene (all sites except R) are the minor possible sources of PAH.

The *F1/F1 + Pyr* isomer pair ratios closely match those determined from few (Benner et al., 1989; Fraser et al., 1998) environmental sources, which include tunnel with light duty gasoline vehicles (at all sites, except R), tunnel with heavy diesel trucks and gasoline vehicles (at TP).

*IP/IP+B[ghi]P* isomer pair (Table 4.6 and Table 4.7) ratio ranged from 0.216-0.582 at TP with a mean of 0.342, 0.225-0.561 with a mean of 0.362 at T/I, 0.162-0.393 with a mean of 0.287 at T-O and from 0.102-0.503 with a mean of 0.425 at rural site. The *IP/IP + B[ghi]P* isomer pair ratios (Table 4.10) show that PAHs in the present study, are derived primarily from petroleum combustion (at

Table 4.7

## Possible PAH sources as determined from PAH isomer pair ratios

Sampling stations	Ac/178 <sup>a</sup>	Fl/Fl + Py <sup>a</sup>	BaA/228 <sup>a</sup>	IP/IP + BghiP <sup>a</sup>
TP	0.487(0.355-0.707)	0.452(0.389-0.482)	0.518(0.343-0.633)	0.342(0.216-0.582)
TI	0.556(0.351-0.726)	0.489(0.371-0.557)	0.555(0.327-0.656)	0.362(0.225-0.561)
TO	0.483(0.238-0.722)	0.486(0.363-0.522)	0.551(0.374-0.614)	0.287(0.162-0.393)
R	0.465(0.368-0.639)	0.349(0.162-0.445)	0.694(0.583-0.821)	0.425(0.102-0.503)
PAH sources	Ac/178 <sup>b</sup>	Fl/Fl + Py <sup>b</sup>	BaA/228 <sup>b</sup>	IP/IP + BghiP <sup>b</sup>
<i>Petroleum/coal fuels</i>				
<i>Kerosene</i>		<b>0.46</b>	<b>0.35</b>	<b>0.48</b>
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	<b>0.26</b>	<b>0.34</b>	<b>0.43</b>	<b>0.39</b>
Lubricating oil		<b>0.29</b>		<b>0.12 (0.00-0.13)</b>
Coal	0.20 (0.00-0.41)			
Asphalt			<b>0.50</b>	<b>0.52-0.54</b>
<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 (ERM 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 fine particulate		0.59 (0.58-0.60)		0.39 (0.31-0.44)
Road dust	0.18	0.42		0.51
Lubricating oil, 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 ERM 1648 and 1649a)	0.08 (0.06-0.09)	0.36 (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).

**Table 4.8: Molecular pair ratios of BaA/228 at Different sites**

BaA/228	Combustion	Petroleum/Fossil fuels	Environmental Samples
0.518 (TP)	Wood 0.46 (0.30-0.54) Bituminous coal 0.34 (0.18-0.50) Diesel 0.38 (0.18-0.69)	Diesel Oil 0.35 (0.12-0.71) Asphalt 0.50	Used engine oil, gasoline passenger car 0.50 Tunnel with light duty gasoline vehicles 0.46 (0.39-0.51) Creoste treated wood piling 0.50 (0.46-0.53)
0.555 (T/I) 0.551 (T-O)	Diesel 0.38 (0.18-0.69) Coal Tar (SRM 1597) 0.54 Wood 0.46 (0.30-0.54)	Diesel Oil 0.35 (0.12-0.71)	Tunnel with heavy diesel trucks and duty gasoline vehicles 0.57(0.53-0.60)
0.694 (R)		Diesel Oil 0.35 (0.12-0.71)	

**Table 4.9: Molecular pair ratios of FI/FI+Pyr at Different sites**

FI/FI+Py	Combustion	Petroleum/Fossil fuels	Environmental Samples
0.452 (TP)	Wood 0.51 (0.41-0.67) Gasoline 0.44 Diesel 0.39 (0.20-0.58) Crude Oil 0.44 (0.42-0.46)	Kerosene 0.46 Diesel Oil 0.26 (0.01-0.47)	Tunnel with light duty gasoline vehicles 0.45 (0.42-0.49) Tunnel with heavy diesel trucks and duty gasoline vehicles 0.42 (0.41-0.44)
0.489 (T/I) 0.486 (T-O)	Bituminous Coal 0.53 (0.48-0.58) Wood 0.51 (0.41-0.67) Diesel 0.39 (0.20-0.58) No.2 Fuel Oil 0.51 (0.47-0.55)	Kerosene 0.46 Diesel Oil 0.26 (0.01-0.47)	Tunnel with light duty gasoline vehicles 0.45 (0.42-0.49)
0.349 (R)	Diesel 0.39 (0.20-0.58)	Diesel Oil 0.26 (0.01-0.47) Lubricating oil 0.34	

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**Table 4.10: Molecular pair ratios of IP/IP+B[ghi]P at Different sites**

IP/IP+BghiP	Combustion	Petroleum/Fossil fuels	Environmental Samples
0.342 (TP) 0.362 (T/I)	Bituminous Coal 0.48 (0.35-0.62) Kerosene 0.37 Diesel 0.35 (0.19-0.50)	Diesel Oil 0.40 (0.25-0.65)	Savanna fire particulate 0.39 (0.31-0.44) Shale Oil 0.39 Tunnel with light duty gasoline vehicles 0.30 (0.26-0.35) Tunnel with heavy diesel trucks and duty 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) Lubricating Oil, rerefined 0.36
0.287 (T-O)	Diesel 0.35 (0.19-0.50)	Diesel Oil 0.40 (0.25-0.65)	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 diesel trucks and duty 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)
0.425 ( R)	Bituminous Coal 0.48 (0.35-0.62) No.2 Fuel Oil 0.47(0.19-0.50)	Diesel Oil 0.40 (0.25-0.65)	Savanna fire particulate 0.39 (0.31-0.44) Urban air (including SRM 1648 and 1649a) 0.40 (0.27-0.48)

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all sites) (Fig. 4.10). Combustion of diesel (at all sites), kerosene combustion (all sites except at TP and R), and bituminous coal (at TP, T/I and R) (Table 4.10) are the probable major sources of PAH at the present sampling sites. Minor occurrences of unburnt diesel oil (at all sites) were also found. Diesel can enter the soil primarily through release from diesel-powered vehicles. The *IP/IP + B[ghi]P* isomer ratios for the samples closely match those determined from environmental samples that include savanna fire particulate (all sites except T-O), shale oil (at TP and T/I), tunnel with light duty gasoline vehicles (at all sites except R), tunnel with heavy duty trucks (at all sites except R) roadway tunnels (at all sites except R), lubricating oil (at TP, T/I) and used engine oil, diesel car, truck and bus (at T-O).

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 soil in the present study, 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) processes during transport and after deposition into soils.

*Conclusion*

- For the airport site,  $\Sigma_{12}$ PAH concentration spanned from 2.394-7.529  $\mu\text{g/g}$  with a mean of  $4.428 \pm 1.447$   $\mu\text{g/g}$ , showing a maximum at Terminal Park (TP) that ranged from 3.131-7.529  $\mu\text{g/g}$  with a mean of  $5.676 \pm 1.655$   $\mu\text{g/g}$  and minimum at Take-Off (T-O) varying from 2.517- 4.661  $\mu\text{g/g}$  with a mean of  $3.487 \pm 0.726$   $\mu\text{g/g}$ .
- The  $\Sigma_{12}$ PAH concentration at the background site (rural site, R) ranged from 1.205 to 2.127  $\mu\text{g/g}$  with a mean of  $1.714 \pm 0.330$   $\mu\text{g/g}$ .
- No consistent temporal variation in the  $\Sigma_{12}$ PAH concentration around the airport was observed.
- Percentage distribution of individual PAH compounds analyzed showed that Pyrene (19-20%) dominated all the sites, followed by Fluoranthene (11-16%) and Dibenzo (a,h) Anthracene (11-16%). Chrysene concentration was least at all sites (average of 3%)
- At the rural site, 3-ring PAHs *Phen* (10%) and *Anth* (8%) were also present in significant proportions. Thus, showing the presence of low molecular weight PAHs at the background site.
- The *B(a)P* concentration ranged from 0.069 to 0.395  $\mu\text{g/g}$  with a mean of  $0.233 \pm 0.099$   $\mu\text{g/g}$  for the airport site. All the sampling sites, showed around 5 % *B(a)P*.
- At all the sites, the *B(a)P* concentration varied linearly with  $\Sigma_{12}$ PAH concentration. Among the airport sites, *B(a)P* concentration was highest at TP and was lowest at T-O.
- At all the sites 4 & 5-ring PAHs were found to be dominant. 4-and 5-ring compounds together accounted for more than 70% of  $\Sigma_{12}$ PAHs at all the sites.
- The  $\Sigma_{12}$ PAH concentrations increased gradually from the take-off side (T-O) of the airport to the terminal park (TP) and attained a maximum value at TP.

Hence, PAH level was minimum in the soils of take-off side while it was comparatively higher at taxi/idle side (T/I) and finally reached maximum at TP.

- $\Sigma_{12}$ PAH concentration for the airport site was found to be 2.58 times higher to that at the rural site.
- The concentration of PAHs around the IGI Airport was found to be higher as compared to the concentration reported in airport soils from other countries.
- The preliminary results showed combustion could be the major contributing source to the PAH load around the airport.
- In order to have a comprehensive picture of PAH sources and their spatial and temporal variation in soils of an airport in Delhi, a detailed study is required.

## *Bibliography*

- Abbott DW, Moody RL, Mann RM, and Vo-Dinh T (1986)** Synchronous luminescence screening for Polynuclear aromatic compounds in environmental samples collected at a coal gasification process development unit. *Am Ind Hyg Assoc J*, 47: 379-385
- Aceves, M. and Grimalt, J. O. (1993) Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. *Environ. Sci. Technol.* 27, 2896-2908.
- Allen, J. O., Dookeran, N. M., Smith, K. A., Sarofim, A. F., Taghizadeh, K., and Lafleur, A. L. (1996) Measurement of Polycyclic Aromatic Hydrocarbons Associated with Size-Segregated Atmospheric Aerosols in Massachusetts. *Environ. Sci. Technol.* 30, 1023-1031.
- Amagai, T., Takahashi, Y., and Matsushita, H. (1999) A survey on polycyclic aromatic hydrocarbon concentrations in soil in Chiang-Mai, Thailand. *Environmental International*, 25, 5, 563-572.
- Ambient Air Pollution, PAH Position Paper, July 27<sup>th</sup> 2001.
- Anderson, C. William, Research Needs related to improving air emissions from Diesel Engines, Gas turbines and ordnance, American Academy of Environmental Engineers, Annapolis, 1999. ([www.aeee.net](http://www.aeee.net)).
- ATSDR-Public Health Assessment, Commencement Bay, South Tacoma Field, Washington, U. S. A., March 2006. ([www.astdr.cdc.gov/HAC/PHA](http://www.astdr.cdc.gov/HAC/PHA)).
- Baek, S. O., Field, R. A., Goldstone, M. E., Kirk, P. W., Lester, J. N., and Perry, R., (1991), A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate, and behavior, *Water Air Soil Pollut.*, 60, 279-300.
- Baek SO, Goldstone ME, Kirk PWW, Lester JN, and Perry R (1992) Concentrations of particulate and gaseous polycyclic aromatic hydrocarbons in London air following a reduction in the lead content of petrol in the United Kingdom. *Sci Total Environ*, 111: 169-199.

- Baker, J. E., and Eisenreich, S. J. (1990) Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior, *Environ. Sci. Technol.*, 24,342-352.
- Bakkera, M. I. U, Casadob, B., Koerselmana, J. W., Tolls, J., Kolloffela, C. (2000) Polycyclic aromatic hydrocarbons in soil and plant samples from the vicinity of an oil refinery, *The Science of the Total Environment* 263, 91-100
- Basheer, C., Obbard, J.P. and Lee, H.K. (2003) Persistent Organic Pollutants in Singapore's Coastal marine environment: Part II, Sediments. *Water, Air, and Soil Pollution* 149:315–325.
- Baumard, P., Budzinski, H. and Garrigues, P. (1998) Polycyclic aromatic hydrocarbons in sediments and mussels of the Western Mediterranean Sea. *Environ. Toxicol. Chem.* 17, 765–776.
- Becher G and Bjorseth A (1983) Determination of exposure to polycyclic aromatic hydrocarbons by analysis of human urine. *Cancer Letters*, 17: 301-311.
- Benner BA Jr, Gordon GE, and Wise SA (1989) Mobile sources of atmospheric polycyclic aromatic hydrocarbons: a roadway tunnel study. *Environ Sci Technol*, 23: 1269-1278.
- Bernabei, M., Reda, R., Galiero, R., Bocchinfuso, G., (2003) Determination of total and Polycyclic Aromatic Hydrocarbons in aviation jet fuel, *Journal of Chromatography A*, 985,197-203.
- Bjorseth, A. (1977) Analysis of polycyclic aromatic hydrocarbons in particulate matter by glass capillary gas chromatography. *Anal. Chim. Acta* 94, 21–27.
- Bogovski P, M., Kunte H, 8 Walker EA eds. Environmental carcinogens - Selected methods of analysis, Vol 3 - Analysis of polycyclic aromatic hydrocarbons in environmental samples. Lyon, *International Agency for Research on Cancer*, pp 155-162 (IARC Publications No 29).
- Borneff J & Kunte H (1979) Method 1 - Analysis of polycyclic aromatic hydrocarbons in water using thin layer chromatography and spectrofluorometry. In: Egan H,



- Castegnaro M, Bogovski P, Kunte H, & Walker EA eds. *Environmental carcinogens - Selected methods of analysis*, Vol 3 - Analysis of polycyclic aromatic hydrocarbons in environmental samples. Lyon, International Agency for Research on Cancer, pp 129-139 (IARC Publications No 29).
- Bouloubassi, I., Fillaux, J. and Saliot, A. (2001) Hydrocarbons in Surface' Sediments from the Changjiang (Yangtze River) Estuary, East China Sea. *Marine Pollution Bulletin* 42(12), pp. 1335-1346.
- Bryselbout, C., Henner, P., Carsignol, J., Lichtfouse, (2000) PAHs in highway plants and soils. Evidence for a local distillation effect, *Analisis*, 28, N° 4, EDP Sciences, Wiley-VCH 2000
- Bucheli, T. D., Blum, F., Desaulles, A., Gustafsson, O. (2004) Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere* 56, 1061–1076.
- Budzinski, H., Jones, I., Bellocq, J., Pie L rard, C., Garrigues, P., (1997), Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Mar.Chem.*,58, 85–97.
- Business line, July 10, 2004.
- Butler J. D., Butterworth, V., Kellow, S. C., and Robinson, H. G., (1984), Some observations on the Polycyclic Aromatic Hydrocarbon (PAH) content of surface soils in Urban areas, *The Science of the Total Environment*, 33,75-85.
- Butler A. C., Sibbald R. R. (1986) Isolation and Gas-Chromatographic Determination of Saturated and Polycyclic Aromatic Hydrocarbons in Mussel. *Bull. Environ. Toxicol.*37,570–578.
- Caricchia, A. M., Chiavarini, S., Pezza, M., (1999) Polycyclic aromatic hydrocarbons in the atmospheric particulate matter in the city of Naples Italy, *Atmospheric Environment* 33: 3731-38.
- Chaudhry, G. R. (1994) *Biological Degradation and Bioremediation of Toxic Chemicals*, Dioscorides Press, Portland, OR, U.S.A.

- Chen Baoliang, (2004) Distributions of PAHs in surface waters, sediments and soils of Hangzhou City, China, *Water Research*, 38, 3558-3568.
- Chen, L., Ran Y., Xing B., Mai B., He J., Wei X., Fu J., Sheng G., (2005) Contents and sources of PAHs and organochlorine pesticides in vegetable soils of Guangzhou, China, *Chemosphere*, 60 (2005) 879-890
- Christensen, E.R., Li, A., Ab Razak, I.A., Rachdawong, P., and Karls, J.F.(1997) Sources of polycyclic aromatic hydrocarbons in sediments of the Kinnickinnic River, Wisconsin. *J Great Lakes Res* 23(1), 61–73.
- Chu S. G., Liu, H., Ma L. L., Xu, X. B., (2003), PAHs in soils adjacent to Highways in Beijing, People's Republic of China, *Environmental Contamination and Toxicology*, 70, 972-977.
- Chuang, Jane, 1996, Analysis of soil and Dust for Polycyclic Aromatic Hydrocarbons, USEPA Project Summary, 1996.
- Cirillo, R. R., Tschanz, J.F & Camaioni, J. E., (1975), An evaluation of strategies for airport air pollution control. Argonne, US Argonne National Laboratory, Report No. ANL/ES-45.
- Clark, A. I, McIntyre, A. E., Perry, R., & Lester, J. N. (1983) Air Quality Measurements in the Vicinity of Airports, *Environmental Pollution (Series B)* 6 (1983) 245-261.
- Crepineau C., Rychen, G., Feidt, C., Roux, Y. L., Lichtfouse, E., and Laurent, F., (2003), Contamination of Pastures by PAHs in the vicinity of a Highway, *J. Agric. Food Chem*, 51,4841-4845.
- Dennis MJ, Massey RC, McWeeny, Knowles ME, and Watson D (1983) Analysis of polycyclic aromatic hydrocarbons in UK total diets. *Fd Chem Toxic*, 21: 569-574
- Doong,R. and Lin,Y.(2004) Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan. *Water Research* 38,1733–1744

- Ducoulombier and Rychen (2003) Assessment of soil and grass PAH contamination levels in agricultural fields located near a motorway and an airport, *Agronomie* 23 (2003) 345-348.
- ENVIRON International Corporation, New Jersey for City of Park Ridge, Illinois (2000) Preliminary study and analysis of toxic air pollutant emissions from O'Hare International Airport and the resulting Health risks created by these toxic emissions in surrounding residential communities.
- Fraser, M.P., Cass, G.R., Simoneit, B.R., and Rasmussen, R.A. (1998b) Air quality model evaluation data for organics. 5. C6–C22 nonpolar and semipolar aromatic compounds. *Environ.Sci. Technol.* 32, 1760–1770.
- Gadzala, R.M., and Busjewski, B. (1995) Properties and determination of polycyclic aromatic hydrocarbons (PAHs) using chromatographic methods. *Polish Journal of Environmental Studies* 4(1), 5-15.
- GAO Report, Aviation and the Environment- Strategic Framework to Address Challenges posed by Aircraft Emissions, Feb 2003.
- Garcia-Alonso, S., Perez-Pastor, R.M. and Sevillano-Castano, M.L., (2003) Occurrences of PCBs and PAHs in an Urban Soil of Madrid (Spain), *Toxicol. And Environ. Chem.*, 2003, Vol. 85, Nos. 4-6, pp. 193-202.
- Garrigues,P., & Ewald, M. (1987) High resolution emission spectroscopy (Shopl'skii effect) :a new analytical technique for the analysis of polycyclic aromatic hydrocarbons (PAH) in the environmental samples. *Chemosphere* 16(2/3), 485-494.
- Griest WH and Caton JE (1983) Extraction of polycyclic aromatic hydrocarbons for quantitative analysis. In: Bjorseth A ed. *Handbook of polycyclic aromatic hydrocarbons*. New York, Marcel Dekker, Inc, pP 95-148.
- Grimmer G and Bonke H (1979a) Method 3 - Gas chromatographic profile analysis of polycyclic aromatic hydrocarbons in lubricating oil, cutting oil and fuel. In: Egan H, Castegnaro

- Grimmer G and Bonke H (1979b) Method 4 - Gas chromatographic profile analysis of polycyclic aromatic hydrocarbons in (I) high protein foods, (II) fats and vegetable oils and (III) plants/soils and sewage sludge. In: Egan H, Castegnaro M, Bogovski P, Kunte H, and Walker EA eds. Environmental carcinogens - Selected methods of analysis, Vol 3 - Analysis of polycyclic aromatic hydrocarbons in environmental samples. Lyon, *International Agency for Research on Cancer*, op 163-173 (IARC Publications No 29).
- Grimmer G (1983) Profile analysis of PAH in air. In: Handbook of Polycyclic aromatic hydrocarbons. Eds, Bjorseth A, Marcell Dekker Inc, New York. Pp. 149-183.
- Hawthorne SB and Miller DJ (1987) Extraction and recovery of polycyclic aromatic hydrocarbons from environmental solids using supercritical fluids. *Anal Chem*, 59: 1705-1708.
- Hawthorne SB, Krieger MS and Miller DJ (1989a) Supercritical carbon dioxide extraction of polychlorinated biphenyls, polycyclic aromatic hydrocarbons, heteroatom-containing polycyclic aromatic hydrocarbons, and n-alkanes from polyurethane foam sorbents. *Anal Chem*, 61: 736-74n
- Hawthorne SB, Miller DJ, and Krieger MS (1989b) Coupled SFE-GC: a rapid and simple technique for extracting, identifying, and quantitating organic analytes from solid and sorbent resins. *J Chromatogr Sci*, 27: 347-354.
- Hindustan Times, 4 Feb, 2006
- Hoffman, E. J., Mills. G. L., Latimer, J. S., and Quinn, J. G. (1984) Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. *Environ. Sci. Technol.* 18,580.
- Hong, H., Xu, L., Zhang, L., Chen, J.C., Wong, Y.S., and Wan, T.S.M., (1995) Environmental fate and chemistry of organic pollutants in the sediments of Xiamen and Victoria Harbours. *Marine Pollution Bulletin*, 31, 229-236.
- Howard J (1979) Method 5 - Analysis of benzo[a]pyrene and other polycyclic aromatic hydrocarbons in foods. In: Egan H, Castegnaro M, Bogovski P,

- Kunte H, and Walker EA eds. Environmental carcinogens -Selected methods of analysis, Vol 3 - Analysis of polycyclic aromatic hydrocarbons in environmental samples. Lyon, *International Agency for Research on Cancer*, pp 175-191 (IARC Publications No 29).
- Howard PC, Hecht SS, and Beland FA eds. (1990) Nitroarenes - Occurrence, metabolism, and biological impact. New York, Plenum Press.
- <http://delhairport.com>
- <http://en.wikipedia.org/wiki/Delhi#Airports>
- <http://www.anr.state.vt.us/dec/wastediv/sms/Clarendon/Chemicals.found.presentation.text.doc>
- IARC, 1983. IARC Working Group (1983) *Polynuclear Aromatic Hydrocarbons. Part 1. Chemical, Environmental and Experimental Data*. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. International Agency for Research on Cancer, Lyons 32, 1—477.
- IUPAC (1987) International Union of Pure and Applied Chemistry-Recommended method for a thin- layer- chromatography screening method for the determination of benzo[a]pyrene in smoked food (prepared for publication by Grimmer, G. and Jacob, J.). *Pure & Appl Chem*, 59(12), 1735-1738.
- Jacob J and Grimmer G (1979) Extraction and enrichment of polycyclic aromatic hydrocarbons (PAH) from environmental matter. In: Egan H, Castegnaro M, Bogovski P, Kunte H, and Walker EA eds. *Environmental carcinogens - Selected methods of analysis*, Vol 3 - Analysis of polycyclic aromatic hydrocarbons in environmental samples. Lyon, International Agency for Research on Cancer, pp 79-89 (IARC Publications No 29).
- Johnston, W., and Harrison, R. M., (1984), Deposition of metallic and organic pollutants along the M6 motorway, *Sci. Tot. Environ.* 33, 119-127

- Jones KC, Stratford JA, Waterhouse, and Vogt NB (1989) Organic contaminants in Welsh soils: polynuclear aromatic hydrocarbons. *Environ Sci Technol.* 23: 540-550.
- Jones, K. C., Stratford, J. A., Tidridge, P., Waterhouse, K. S., and Johnston, A. E., (1989b), Polynuclear aromatic hydrocarbons in an agricultural soil soil: long-term changes in profile distribution. *Environ. Pollut.* 56, 337-351.
- Jones, K. C., Stratford, J. A., Waterhouse, K. S., Furlong, E. T., Giger, W., Hites, R. A., Schaffner, Ch., and Johnston, A. E., (1989c), Increases in the polynuclear aromatic hydrocarbons content of an agricultural soil over the last century. *Environ. Sci. Technol.*, 23, 95-101
- Jones, K. C., Stratford, J. A., Waterhouse, K. S., Vogt, N. B., (1989d), Organic contaminants in Welsh soils, polynuclear aromatic hydrocarbons, *Environ. Sci. Technol.*, 23, 540-550
- Jordan, B. C., (1977), an assessment of potential air quality impact on general aviation. Research Triangle Park, NC, Environmental Protection Agency, Office of Air Quality Planning and Standards.
- Kordybach, Terelak, 1998, Content of PAHs in arable soils in Poland, presented at the 4<sup>th</sup> International symposium and exhibition on Environmental contamination in central and Eastern Europe, Warsaw 1998.
- Kristin Rypdal , Aircraft Emissions - Good practice guidance and uncertainty management in national Greenhouse Gas Inventories, (Statistics Norway), ([www.ipcc-hggip.iges.or.jp](http://www.ipcc-hggip.iges.or.jp)).
- Kveseth, K. and Sortland, B. (1982) Polycyclic aromatic hydrocarbons in sewage, mussels and tap water. *Chemosphere* 11(7), 623–639.
- LaFlamme, R.E., and Hites, R.A. (1978) The global distribution of polycyclic aromatic hydrocarbons in recent sediments. *Geochimica et Cosmochimica Acta* 42, 289–303.

- Lane DA (1989) The fate of polycyclic aromatic compounds in the atmosphere and during sampling. In: Vo-Dinh T ed. *Chemical analysis of polycyclic aromatic compounds*. New York, John Wiley and Sons, pp. 31-58.
- Langenfeld JL, Hawthorne SB, Miller DJ, and Pawliszyn J (1993) Effects of temperature and pressure on supercritical fluid extraction efficiencies of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Anal Chem*, 65: 338-344
- Lee ML, Novotny MV, and Bartle KD (1981) *Analytical chemistry of polycyclic aromatic compounds*. New York, Academic Press.
- Leister, D. L. and Baker, J. E. (1994) *Atmos. Environ.* 28, 1499-1520.
- Lenicek J., Sekyra M., Pandey P., Citkova M., Benes I., Novotna J., Kocianova S., Helaskova J., Simonova A. (1997) Polycyclic aromatic hydrocarbons at "Program Teplice" sites in the Czech Republic. *Toxicol. Environm. Chem.* 58, 25.
- Liu, M., Baugh, P.J., Hutchinson, S.M., Yu, L. and Xu, S. (2000). Historical record and sources of polycyclic aromatic hydrocarbons in core sediments from the Yangtze Estuary, China. *Environmental Pollution* 110, 357-365
- Lockhart, W. L., Wagemann, R., Tracey, B., Sutherland, D. Thomas, D. J. (1992) Presence and implications of chemical contaminants in the freshwaters of the Canadian Arctic. *Sci. Tot. Environ.* 122, 165-243.
- Luca, G.D., Furesi, A., Leardi, R., Micera, G., Panzanelli, A., Piu, P.C., and Sanna, G. (2004) Polycyclic aromatic hydrocarbons assessment in the sediments of the Porto Torres Harbor (Northern Sardinia, Italy). *Marine Chemistry* 86, 15-32.
- Ma, L. L., Chu, S. G., Xu, X. B., (2003), Organic contamination in the greenhouse soils from Beijing suburbs, China, *J. Environ. Monit.* 5, 786-790.

- Ma L. L., Chu, S. G., Wang, X. T., Cheng, H. X., Liu, X. F., Xu, X. B., (2005), PAHs in the surface soils from outskirts of Beijing, China, *Chemosphere* 58 (2005) 1355-1363.
- Macias-Zamora, J.V., Mendoza-Vega, E. and Villaescusa-Celaya, J.A. (2002) PAHs composition of surface marine sediments: a comparison to potential local sources in Todos Santos Bay, B.C., Mexico. *Chemosphere* 46(3), 459-468.
- Mackay, D., Shiu, W. Y. and Ma, K. C. (1992) Illustrated Handbook of Physico-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. II Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans. Lewis Publishers, Boca Raton, p.597.
- Mai, B., Fu, J., Zhang, G., Lin, Z., Min, Y., Sheng, G., and Wang, X. (2001) *Appl. Geochem.* 16, 1429-1445.
- Mai, B., Qi, S., Zeng, E.Y., Yang, Q., Zhang, G., Fu, J., Sheng, G., Peng, P. and Wang, Z. (2003) Distribution of Polycyclic Aromatic Hydrocarbons in the Coastal Region off Macao, China: Assessment of Input Sources and Transport Pathways Using Compositional Analysis. *Environ. Sci. Technol.* 37,4855-4863.
- Malawska M. and Wilkomirski B. (2000) An Analysis of Soil and Plant (*Taraxacum officinale*) Contamination with Heavy metals and PAHs in the area of the Railway Junction Ilawa Glowna, Poland, *Water, Air and Soil Pollution*, 127, 339-349.
- Maldonado, C., Bayona, J.M., Bodineau, L. (1999) Sources, distribution, and water column processes of aliphatic and polycyclic aromatic hydrocarbons in the Northwestern Black Sea water. *Environ Sci Technol* 33, 2693-2702.
- Maliszewska-Kordybach, B. (1996) PAHs in agricultural soils in Poland: preliminary proposals of criteria to evaluate the level of soil contamination, *Applied Geochemistry*, 11, 121-127.



- Malisewska-Kordyback and Terelak, (1998) Content of PAHs in arable soils in Poland, IV<sup>th</sup> International Symposium and exhibition on Environmental contamination in Central and Eastern Europe, *Warsaw*
- Maliszewska-Kordybach, B. and Smreczak, B. (2000) Ecotoxicological activity of soils polluted with Polycyclic aromatic hydrocarbons (PAHS)- Effect on plants, *Environmental technology*, 21, 1099-1110
- Marcus, J.M., Swearingen, G.R., Williams, A.D., Heizer, D.D. (1988) Polynuclear aromatic hydrocarbon and heavy metal concentrations in sediments of coastal South Carolina marinas. *Archives of Environmental Contamination and Toxicology* 17, 103– 113.
- Martens, D., Maghun, J., Spitzauer, P. and Kettrup, A., (1997), Occurrence and distribution of PAHs in an agricultural ecosystem, *Fresenius J Anal Chem* (1997) 359: 546-554.
- Maskaoui, K., Zhou, J.L., Hong, H.S. and Zhang, Z.L. (2002) Contamination by polycyclic aromatic hydrocarbons in the Jiulong river estuary and Western Xiamen sea, China. *Environmental pollution* 118, 109-122
- McCready, S., Slee, D.J., Birch, G.F. and Taylor, S.E. (2000) The Distribution of Polycyclic Aromatic Hydrocarbons in Surficial Sediments of Sydney Harbour, Australia, *Marine Pollution Bulletin* 40(11), 999-1006
- McVeety, B.D., and Hites, R.A. (1988) Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. *Atmos. Environ.* 22, 511–536.
- Meharg, A. A., Wright, J., Dyke, H., Osborn, D., (1998), Polycyclic aromatic hydrocarbon (PAH) dispersion and deposition to vegetation and soil following a large-scale chemical fire. *Environ. Pollut.* 99, 29-36.
- Menichini E, Bonanni L, and Merli F (1990) Determination of polycyclic aromatic hydrocarbons in mineral oils and oil aerosols in glass manufacturing. *Toxicol Environ Chem*, 28: 37-51.

- Menichini E, di Domenico A, Bonanni L, Corradetti E, Mazzanti L, and Zucchetti G (1991) Reliability assessment of a gas chromatographic method for polycyclic aromatic hydrocarbons in olive oil. *J Chrom*, 555: 211-220.
- Menichini E (1992a) Urban air pollution by polycyclic aromatic hydrocarbons: levels and sources of variability. *Sci Total Environ*. 116: 109-135
- Murray JJ, Pottie RF, and Pupp C (1974) The vapor pressures and enthalpies of sublimation of five polycyclic aromatic hydrocarbons. *Can J Chem*, 52: 557-563.
- Nadal. M, Schuhmacher M., Domingo J.L. (2004) Levels of PAHs in soil and vegetation samples from Tarragona County, Spain, *Environmental Pollution* 132, 1-11.
- Nam, J.J., Song, B.H., Eom, K.C., Lee, S.H., and Smith, A. (2003), Distribution of PAHs in agricultural soils in South Korea, *Chemosphere* 50 (2003) 1281-1289.
- Natusch DFS and Tomkins BA (1978) Isolation of polycyclic organic compounds by solvent extraction with dimethyl sulfoxide. *Anal Chem*, 50: 1429-1434.
- Oanh, N. T. K., Reutergardh, L. B. and Dung, N. T. (1999) Emission of polycyclic aromatic hydrocarbons and particulate matter from domestic combustion of selected fuels. *Environ. Sci. Technol.* 33, 2703–2709.
- Ogunfowokan, A.O., Asubiojo, O.I. and Fatoki, O.S. (2003) Isolation and determination of polycyclic aromatic hydrocarbons in surface runoff and sediments. *Water, Air, and soil Pollution* 147, 245-261.
- Oros and Ross, 2004; Oros, D.R., and Ross, J.R.M. (2004) Polycyclic aromatic hydrocarbons in San Francisco Estuary sediments. *Marine Chemistry* 86, 169– 184.
- PAH position paper, 2001

- Pandey, P.K., Patel, K.S. and Lenicek, J. (1999) Polycyclic Aromatic Hydrocarbons: need for assessment of health risks in India?. *Environmental Monitoring and Assessment* 59, 287–319.
- Park, K., Sims, R. C., Dupont, R. R., Doucette, W. J., and Mathews, J. E., (1990), Fate of polycyclic aromatic hydrocarbon compounds in two soil type: Influence of volatilization, abiotic loss and biological activity. *Environ. Toxicol. Chem.* 9, 187-195, 1990.
- Parlanti, E. (1990) Utilisation des hydrocarbures comme traceurs d'origine de la matière organique sédimentaire en milieu marin. Etude du Golfe du Lyon et du Golfe de Gascogne (Programme Ecomarge) PhD thesis Nr 495, University Bordeaux I, Bordeaux, France; 289 pp.
- Pathirana, S., Connell, D. W., and Vowles, P. D. (1994) Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in an Urban Roadway System, *Ecotoxicology and Environmental Safety*, 28, 256-269.
- Peters, A. J., Gregor, D. J., Teixeira, C. F., Jones, N. P., and Spencer, C. (1995) The recent depositional trend of polycyclic aromatic hydrocarbons and elemental carbon to the Agassiz Ice Cap, Ellesmere Island, Canada. *Sci. Tot. Environ.* 161, 167–179.
- Prahl, F. G. and Carpenter, R. (1983) Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington Coastal sediments. *Geochimica et Cosmochimica Acta* 47, 1013-1023.
- Quilliam MA and Sim PG (1988) Determination of polycyclic aromatic compounds by high performance liquid chromatography with simultaneous mass spectrometry and ultraviolet diode array detection. *J Chromatogr Sci*, 26: 160-167.
- Ramdhal T, Becher G and Bjorseth A. (1982) Nitrated Polycyclic aromatic hydrocarbons in urban air particles. *Environ. Sci. Technol.* 16, 861-865.

- Readman, J.W., Mantoura, R.F.C., Rhead, M.M., Brown, L., (1982) Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH) in the Tamar Estuary. *Estuarine Coastal Shelf Science* 14, 369-386.
- Readman, J.W., Mantoura, R.F.C., and Rhead, M.M. (1984) The physico chemical speciation of polycyclic aromatic hydrocarbons in aquatic systems. *Fresenius Journal of Analytical Chemistry* 319,126-131.
- Robertson, D.J., Groth, R.H. and Blasko, J.J. (1980) Organic content of particulate matter in turbine engine exhaust. *J.Air Pollut. Control Ass.*, 30, 261-6.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1993) Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy duty diesel trucks. *Environ Sci Technol* 27, 636- 651.
- Roy, Irwin J., (1997) Environmental contaminants encyclopedia, Jet Fuel 5 entry, July 1997, National Park Service.
- Saber A, Jarosz J, Martin-Bouyer M, Paturel L, and Vial M (1987) Analysis of polycyclic aromatic hydrocarbons in lacustral sediments by high resolution Shpol'skii spectrofluorimetry at 10 K. *Intern J Environ Anal Chem*, 28: 171-184.
- Sanders, M., Sivertsen, S. and Scott, G. (2002) Origin and distribution of polycyclic aromatic hydrocarbons in surficial sediments from the savannah river. *Arch Environ Contam Toxicol* 43(4), 438-48.
- Santodanto, J., Howard, P., & Basu, D. (1981) Health and ecological assessment of polynuclear aromatic hydrocarbons. *J Environ Pathol Toxicol* 5(1), 1-364
- Schauer, J.J., Kleeman, M.J., Cass, G.R., and Simoneit, B.R.T. ( 2002) Measurement of emissions from air pollution sources: 5. C1-C32 organic compounds from gasoline-powered motor vehicles. *Environ Sci Technol* 36, 1169-1180.

- Schauer, J.J., Kleeman, M.J., Cass, G.R., and Simoneit, B.R.T. (1999) Measurement of emissions from air pollution sources: 2. C1 through C30 organic compounds from medium duty diesel trucks. *Environ Sci Technol* 33, 1578–1587.
- Shabad, L. M., Cohan, Y., Ilnitsky, A.P., Khesina, A. Ya., Shcherbak, N.P., and Smirnov, G.A., (1971) The Carcinogenic Hydrocarbon Benzo(a) Pyrene in Soil, *J. of the National Cancer Institute*, Vol 47, No. 6, pp. 1179-1191.
- Shabad, L. M and Smirnov, G.A, (1972) Aircraft engines as a source of carcinogenic pollution of the environment, *Atmospheric Environment*, 1972, Vol. 6, pp 153-164.
- Shabad, L. M. and Smirnov, G.A. (1976) IARC Scientific Publication, INSERM, 52, 53-60.
- Shabad, L. M, (1980) Circulation of carcinogenic PAHs in the human environment and cancer prevention, *J. National Cancer Institute*, Vol. 64, No. 3, pp. 405-410.
- Short, J. W., Kvenvolden, K. A., Carlson, P. R., Hostettler, F. D., Rosenbauer, R. J. and Wright, B. A. (1999) Natural background in Benthic sediments of prince William sound, Alaska: Oil versus Coal. *Environ. Sci. Technol.* 33, 34–42.
- Shumway, L.A. (2000) Technical Report 1845, December 2000, Trace Element and Polycyclic Aromatic Hydrocarbon Analyses of Jet Engine Fuels: Jet A, JP5, and JP8.
- Sims RC and Overcash (1983) Fate of Polynuclear aromatic compounds (PNAs) in soil plant systems. *Residue Reviews*, 88: 1-68.
- Skrbic, B., Cvejanov, J., and Mladenovic, M. D. (2005) PAHs in surface soils of Novi Sad and Bank sediment of the Danube River, *Journal of Environmental Science and Health*, A40: 29-42.
- Soclo, H.H., Garrigues, Ph. and Ewald, M. (2000) Origin of Polycyclic Aromatic Hydrocarbons (PAHs) in Coastal Marine Sediments: Case Studies in Cotonou (Benin) and Aquitaine (France) Areas. *Marine Pollution Bulletin* 40, 387-396.

- Spitzer T and Kuwatsuka S (1986) Simple method for determination of polynuclear aromatic hydrocarbons in soil by clean up on XAD-2. *J Chromatogr*, 358: 434-437
- Spitzer, T., and Kuwatsuka, S., 1993, Residue levels of polynuclear aromatic compounds in urban surface soil from Japan, *Journal of Chromatography*, 643 (1993) 305-309.
- Stockham, J. D., Luebcke, E. H. & Taubenkibel, L. (1979) Aircraft turbine engine Particulate emission characterization. Proc. Air Quality and Aviation: An International Conference, 16-18 October, 1978, Reston, Virginia. Washington, DC, US Federal Aviation Administration, FAA-EE-78-26, 27-43
- Stout P and Mamantov G (1989) Recent advances in infrared analysis of polycyclic aromatic compounds. In: Vo-Dinh T ed. *Chemical analysis of polycyclic aromatic compounds*. New York, John Wiley and Sons, pp 411-432.
- Takashi, A., Yukari, T., and Matsushita, H., (1999) A survey on PAHs in soil in Chiang-Mai, Thailand, *Environmental International*, 25. 563-572.
- Tao, S., Cui, Y.H., Xu, F.L., Li, B.G, Cao, J., Liu, W.X., Schmitt, G., Wang, X.J., Shen, W.R., Qing, B.P., Sun, R, (2004) *The Science of the Total Environment* 320, 11-24.
- The Financial Express, 22 Feb, 2006
- Thomas, D., (1989) Aircraft trace element pollution around London Gatwick airport, ([www.areco.org](http://www.areco.org))
- Thrane K.E. and Mikalsen A. (1981) High volume sampling of airborne Polycyclic aromatic hydrocarbons using glass fiber filter and polyurethane foams. *Atmospheric Environment* 15, 909-918.
- Trapido M., (1999) PAHs in Estonian Soil: Contamination and Profiles, *Environmental Pollution*, 105, 1999, 67-74.

- United States Environmental Protection Agency (1977), Impact of new source performance standards on 1985 National emissions from stationary sources. Research Triangle Park, NC, US EPA/450/3-76-917
- URS Corporation for Federal Aviation Administration, Office of Environment and Energy, 2003, Select Resource Materials and Annotated Bibliography on The topic of Hazardous Air Pollutants (HAPs) Associated with Aircraft, Airports and Aviation.
- USEPA, (1996), Method 8000B, Determinative Chromatographic Separations
- Vaessen HA, Jekel AA, Wilbers AA (1988) Dietary intake of polycyclic aromatic hydrocarbons, *Toxicol. Environ. Chem.* 16, 281
- Van Brummelen, T. C., Verweij, R. A., Wedzinga, S. A., and Van Gestel, C. A. M., (1996a), Enrichment of polycyclic aromatic hydrocarbons in forest near a blast furnace plant. *Chemosphere*, 32, 293-314.
- Varanasi, U. (Ed.) (1989) Metabolism of polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment. CRC press Inc. Boca Raton, FL USA.
- Vo-Dinh T, Bruewer TJ, Colovos GC, Wagner TJ, and Jungers RH (1984) Field evaluation of a cost-effective screening procedure for polynuclear aromatic pollutants in ambient air samples. *Environ Sci Technol*, 18: 477-482.
- Vo-Dinh T ed. (1989) *Chemical analysis of polycyclic aromatic compounds*. New York, John Wiley and Sons.
- Vogt, N. B., Brakstad, F., Thrane, K., Nordensen, S., Krane, J., Aamot, E., Kolset, K., Esbensen, K., and Stainness, E., (1987), Polycyclic aromatic hydrocarbons in soil and air: statistical analysis and classification, by the SIMCA method, *Environ. Sci. Technol.*, 21, 35-44.
- Vreuls JJ, De Jong GJ, and Brinkman UATH (1991) On-line coupling of liquid chromatography, capillary gas chromatography and mass spectrometry for the determination and identification of polycyclic aromatic hydrocarbons in vegetable oils. *Chromatographia*, 31: 113-118.

- Wakeham, S.G., Shaffner, C., Giger, W. (1980) Polycyclic aromatic hydrocarbons in recent lake sediments—I. Compounds having anthropogenic origins. *Geochimica et Cosmochimica Acta* 44,405–413.
- Wang Guangdi, Mielke Howard W., Quach Van, Gonzales Chris, Zhang Qiang, (2004) Determination of PAHs and Trace metals in New Orleans Soils and Sediments, *Soils and Sediment Contamination*, 13, 313-327.
- Wehry EL (1983) Optical spectrometric techniques for determination of polycyclic aromatic hydrocarbons. In: Bjorseth A ed. *Handbook of polycyclic aromatic hydrocarbons*. New York, Marcel Dekker, Inc, pp 323-396.
- Weiss P., Riss A., Gschmeidler E., Schentz H., (1994) Investigation of heavy metal, PAH, PCB patterns and PCDD/F profiles of soil samples from an industrialized urban area (Linz, Upper Austria) with multivariate statistical method, *Chemosphere* 29, 9-11.
- Wenclawiak B, Rathmann, and Teuber A (1992) Supercritical-fluid extraction of soil samples and determination of polycyclic aromatic hydrocarbons (PAHs) by HPLC. *Fresenius J Anal Chem*, 344: 497-500.
- White, Russell D., Refining and Blending of Aviation Turbine Fuels, *Drug and Chemical Toxicology*, 22(1), 143-153 (1999).
- Wilcke, W., Zech, W. and Kobz, J., (1996a), PAH pools in soils along a PAH deposition gradient, *Environmental Pollution*, Vol. 92, No.3, pp. 307-313.
- Wilcke, W., Baumler, R., Deschaer, H., Kaupenjohan, M., and Zech, W., (1996b), Small scale distribution of Al, heavy metals, and PAHs in an aggregated Alpine Podzol, *Geoderma* 71, 307-313.
- Wilcke W., Muller S., Kanchanakool N., Nimaskul C., Zech W. (1999a) PAHs in hydromorphic soils of the tropical metropolis Bangkok, *Geoderma*, 91, 297-309.



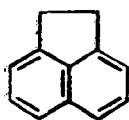
- Wilcke, W., Lilienfein, J., Lima, S. do Carmo and Zech, W., (1999b) Contamination of highly weathered urban soils in Uberlandia, Brazil, *J. Plant Nutr. Soil Sci.* 162, 539-548.
- Wilcke, W., and Amelung, W., (2000), Persistent Organic Pollutants in Native Grassland Soils along a Climosequence in North America, *Soil Sci. Soc. Am. J.* 64:2140-2148,
- Wilcke, Wolfgang, Synopsis, Polycyclic Aromatic Hydrocarbons (PAHs) in Soil - a review, (2000), *J. Plant Nutr. Soil Sci.*, 163, 229-248.
- Wilcock, R. J., Corban, G. A., Northcott, G. L., Wilkins, A. L. and Langdon, A. G. (1996) Persistence of polycyclic aromatic compounds of different molecular size and water solubility in surficial sediment of an intertidal sandflat. *Environ. Toxicol. Chem.* 15, 670-676.
- Wild, S. R., Berrow, M. L., Mc Grath, S. P. and Jones, K. C. (1992) Polynuclear aromatic hydrocarbons in crops from long-term field experiments amended with sewage sludge, *Environ. Pollut.* 76, 25-32.
- Wild SR and Jones KC (1995) Polynuclear Aromatic Hydrocarbons In the United Kingdom environment: a preliminary source inventory and budget. *Environmental Pollution* 88, 91.
- Wilson, S. C., and Jones, K. C., (1993), Bioremediation of soil contaminated with polycyclic aromatic hydrocarbons (PAHs), a review. *Environ. Pollut.* 81, 229-249
- Wise SA (1983) High-performance liquid chromatography for the determination of Polycyclic aromatic hydrocarbons. In: Bjorseth A ed. *Handbook of Polycyclic aromatic hydrocarbons*. New York, Marcel Dekker. Inc, pp 183-256.
- Wise SA (1985) Recent progress in the determination of PAH by high performance liquid chromatography. In: Bjorseth A and Ramdahl T eds. *Handbook of Polycyclic Aromatic Hydrocarbons*, 2. New York, Marca Dekker, Inc, pp 113-191..

- Wright BW and Smith RD (1989) Capillary supercritical fluid chromatography methods. In: Vo-Dinh T ed. *Chemical analysis of polycyclic aromatic compounds*. New York, John Wiley and Sons, pp 111-149.
- Wu, Y., Zhang, J., Zhu, Z. (2003) Polycyclic aromatic hydrocarbons in the sediments of the Yalujiang Estuary, North China. *Marine Pollution Bulletin* 46, 619–625.
- Wu, S. P., Xu, F.L., Dawson, R., Lan, T., Li, B.G., Cao, J., (2005) PAHs in dustfall in Tianjin, China, *Science of the Total Environment*, 345, 115-126
- Wüst, W., Kern, U. and Herrmann, R. (1992) 'Street Washoff Behaviour of Heavy Metals, Polyaromatic Hydrocarbons and Nitrophenols', in *The Fourth International Symposium Highway Pollution Proceedings*, Middlesex Polytechnic, United Kingdom, pp. 265.
- [www.airportindia.org](http://www.airportindia.org)
- [www.average-aerospace.com/html/environment.html](http://www.average-aerospace.com/html/environment.html).
- [www.blonnet.com](http://www.blonnet.com).
- [www.grida.no/climate/ipcc/aviation](http://www.grida.no/climate/ipcc/aviation).
- [www.worldairport.guide.co.uk](http://www.worldairport.guide.co.uk)
- Yamartino, R.J., Smith, D.G., Bremer, S.A., Heinhold, D., Lamich, D. and Taylor, B. (1980), Impact of aircrafts on air quality in the vicinity of airports, US Federal Aviation Administration.
- Yang, S.Y.N., Connell, D.W., Hawker, D.W. and Kayal, S.I. (1991) Polycyclic Aromatic Hydrocarbons in Air, Soil and vegetation in the vicinity of an urban roadway, *The Science of the Total Environment*, 102 (1991) 229-240.
- Yang Y., Zhang X., Korenaga T., (2002) Distribution of PAHs in the soil of Tokushima, Japan, *Water, Air, and Soil Pollution* 138, 51-60.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, *Organic Geochemistry* 33, 489–515.

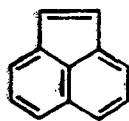
- Zhang ,Z.L., Hong, H.S., Zhou, J.L. and Yu, G. (2004) Phase association of polycyclic aromatic hydrocarbons in the Minjiang River Estuary, China. *The Science of the Total Environment*, 323, 71–86.
- Zhou, J.L., Hong, H., Zhang, Z., Maskaoui, K., Chen, W. (2000) Multi-phase distribution of organic micropollutants in Xiamen Harbour, China. *Water Research* 34, 2132–2150.

## Annexure I

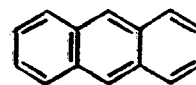
### Structure of the PAHs



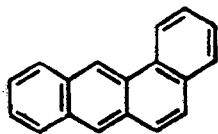
Acenaphthene



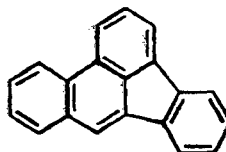
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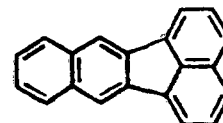
Anthracene



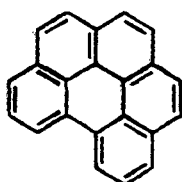
Benz(a)Anthracene



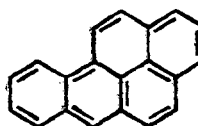
Benz(b)Fluoranthene



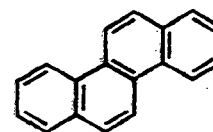
Benz(k)Fluoranthene



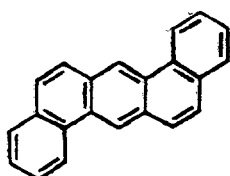
Benz(ghi)Perylene



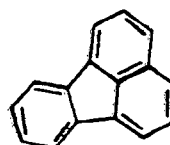
Benz(a)Pyrene



Chrysene



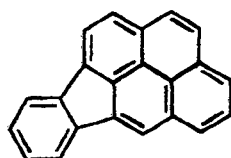
Dibenz(a,h)Anthracene



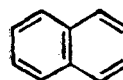
Fluoranthene



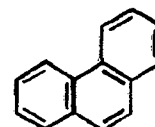
Fluorene



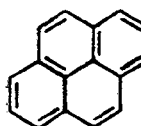
Indeno(1,2,3-cd)Pyrene



Naphthalene



Phenanthrene



Pyrene

