Introduction

POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

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PAHs IN SOIL

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Fate in soil
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Losses of PAHs from the terrestrial environment

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OBJECTIVES
Soil is a great storehouse for minerals, organic matter, water and energy; it is a water filter, a transformer of gases and a gene pool for a huge variety of organisms. Soil, furthermore is a vital for food production, supplying nutrients and water for all plants. Simultaneously, soil is coming increasingly threatened by human activities which reduce its ability to perform its functions. The increasing contamination of soils due to pollutant emission from industries, transport sector and some farm practices can result not only in soil pollution but also in contamination of water and food.

Soils are vital natural resources for the socio-economic development of any country. India is facing a great dilemma between the problems of rapid industrialization, urbanization and the deterioration of soil quality. Today, there are increasing evidences to suggest that a majority of our soil resources are under different degrees of degradation, and are further getting deteriorated at an alarming rate with a risk of jeopardizing human health. Developing strategies to reverse the processes of degradation and to ameliorate the soil quality are the key issues to confront.

Soil ecosystem seems to be the ultimate repository for most of the hydrophobic organic contaminants such as polycyclic aromatic hydrocarbons (PAHs). In recent years, there has been a rapid stride in the field of organic geochemistry, an area of study that deals with circulation of hydrocarbons in the environmental segments. PAHs have received much attention due to their toxicity to humans and their possible harmful effect on soil organisms and plants because of their stability (Menzie et al., 1992). PAHs belong to a ubiquitous group of hazardous organic pollutants which exhibit strong carcinogenic and toxic properties. They are formed by incomplete combustion of fossil fuels and can
enter the soil via atmospheric deposition. PAH enter the soil environment through various anthropogenic sources and can be mobilized in the food chain particularly through the agricultural soils and flood plain soils under cultivation. It is estimated that more than 90% of the total burden of PAH resides in the surface soils (Wild and Jones, 1995).

PAH-soil system has very high information content. On one hand, soils with a solid phase skeleton are a fairly stable medium (compared, for example, with atmospheric air, natural waters, river sediments etc.) in which quite accurate observations can be made. On the other hand, a study of the molecular composition of PAH themselves in soils shows considerable promise for obtaining data on formation pathways of each molecular type and on functional status of the soils (Gennadiyev et al., 1990). The type of land use influences the PAH concentration and patterns in soils depending on the location and the land use. PAH concentration in urban soils is also highly variable because of industry, traffic or specific contamination.

Although, data from animal studies indicate that various PAHs may induce a number of adverse health effects (IARC, 1983; ATSDR, 1995), the main reason for concern about human exposure to these organic compounds is the evidence that several PAHs are carcinogenic. Because PAHs are lipophilic, their deposition on soil and surface waters may also lead to bioaccumulations within the food chain. However, loss of organic pollutants from soil by evaporation or migration/resuspension is a possible source of atmospheric and groundwater contamination and those remaining in soil could also reach adjacent vegetables and wildlife, thus causing direct or indirect exposure of humans to the organic pollutants.
Knowledge of soil contamination with PAH is needed to avoid any food risk and to restrict the deleterious effect of these contaminants on the soil ecosystem (Maliszewska-Kordybach, B., 1996). Contamination of agricultural soil with PAHs creates a serious risk of the introduction of these xenobiotics into human food chain. PAHs present in soil not only create a risk to humans (food contamination, accidental ingestion) but they may exhibit a toxic activity towards different biological elements of the soil environment such as plants, microorganisms etc.

1.1. Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a class of ubiquitous and persistent organic pollutants (POPs) in the environment. They are characterized by their exceptional toxicities towards many living organisms, reluctance in degradations and high lipophilicity, making them a class of very hazardous compounds. Although data from animal studies indicate that various PAHs may induce a number of adverse health effects (IARC, 1983; ATSDR, 1995), the main reason for concern about human exposure to these organic compounds is the evidence that several PAHs are carcinogenic. Some PAHs were found to be very toxic and 16 of them have been identified by US EPA as being toxic, partially mutagenic and carcinogenic "priority pollutants". They represent most of the adverse effects that are caused primarily as a result of anthropogenic activities (Keith and Telliard, 1979).

The International Agency for Research on Cancer (IARC) determined that benzo[a]anthracene and benzo[a]pyrene are probably carcinogenic to humans, while benzo[b]fluoranthene, benzo[j]fluoranthe, benzo[k]fluoranthe, and indeno[1,2,3-c,d]pyrene are possibly carcinogenic to humans (IARC, 1983). In turn, the United States Environmental Protection Agency (US EPA) has classified
the following seven PAHs: benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]-fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene as Group B2, probable human carcinogens (US EPA, 2002).

1.1.1. Nomenclature and Structure of PAHs

PAHs constitute a wide class of compounds composed of carbon and hydrogen atoms arranged in the form of fused benzene rings. They may be composed of unsaturated two, three, four, five, and six-membered rings. Within the group, the compounds range from semi volatile molecules to molecules with high boiling points. The compounds may exist with a great number of structures and, depending on the complexity of the PAHs, in a large number of isomers.

1.1.2. Sources of PAHs in the environment

PAHs originate from natural as well as anthropogenic sources. 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. PAHs emitted in the environment mainly derive from anthropogenic sources. They are formed as by-products of incomplete combustion of fossil fuels, biomass and pyrosynthesis of organic materials. Their occurrence and emissions have therefore been substantial during the past centuries because of the abundant use of fuels for industrial applications, heating, transport, and many other purposes. Thus, PAHs are ubiquitous contaminants in both the general environment and in certain working environments (IARC 1983, 1984a, b, 1985).

The most significant anthropogenic sources of PAH include heat and power generation from coal and other fossil fuels, coal production, petroleum refining, coal and oil shale conversion, and chemical manufacturing (Suess, 1976).
It is believed that combustion processes, including thermal combustion conditions, fuel/stove types and even burning stages, are responsible for the abundance and profiles of PAHs that enter the environment (Chen et al., 2005). Of the combustion-derived PAHs, the low molecular weight (LMW) (three rings) species are abundantly produced at low to moderate temperatures, such as wood and coal combustion. On the contrary, high molecular weight (HMW) (four and more rings) PAHs are generated at high temperatures, such as vehicle emission (Mastral and Callen, 2000). Some PAHs can also be derived from biogenic precursors such as pigments and steroids (Wakeham et al., 1980).

1.1.3. Formation of PAHs

Most prominent source of PAHs in the environment is the incomplete combustion of organic material. During combustion, the organic compounds present in the fuel are fragmented into smaller unstable molecules (free radicals) that can react, through a number of different chemical pathways, to produce the first aromatic ring (Ritchter and Howard, 2000). Further reaction of this aromatic ring with small molecules (2 to 3 carbons; e.g., C₂H₂-acetylene) leads to growth of the aromatic system and formation of larger and more stable multi-ring structures. It is well established that mechanisms of formation of PAHs and of soot are closely intertwined (Macadam, 1997; Ritcher and Howard, 2000; Wal et al., 1997) with high-molecular-weight PAHs (~500–1000 atomic mass units) functioning as molecular precursors of soot particles (Ritcher and Howard, 2000).

There is general agreement that similar qualitative mixtures of PAHs are produced regardless of the type of fuel used (Jenkins et al., 1996; Ramdahl et al., 1982). Parent PAHs with 3, 4, and 5 rings dominate emissions from both wood-burning and vehicle exhaust, as larger molecules have a higher tendency to be
incorporated into soot particles (Ritcher and Howard, 2000). The assemblage of PAHs emitted by different sources apparently varies only slightly; however burning conditions can significantly influence the amount of each PAH produced. Hence, the relative proportion of PAHs from a single fuel source can vary widely (Jenkins et al., 1996; Masclet et al., 1987; Ramdahl et al., 1982).

The type of fuel burnt directly influences the growth mechanism of PAHs and, therefore, the amount released during combustion. PAH emissions do not necessarily have to resemble the original fuel. Automobile emissions encompass a mixture of PAHs derived from several compartments including: (a) PAHs initially present in the fuel; (b) PAHs formed during combustion; (c) PAHs accumulated in the lubricating oil; and (d) PAHs accumulated in the exhaust system (Acres et al., 1982; Marr et al., 1999; Pruell and Quinn, 1988; Schauer et al., 2002). The type of engine (spark ignition, diesel), age of the vehicle, presence of a catalytic converter, vehicle speed, and cold versus hot starts are factors that affect PAHs emissions (Acres et al., 1982; Maricq et al., 1999; Pedersen et al., 1980; Rogge et al., 1993; Schauer et al., 2002).

The molecular distribution of PAHs has also been linked to the temperature at which these compounds are formed. Low temperatures, such as in forest fires and cigarettes, generate mixtures enriched in alkyl-substituted PAHs, whereas higher temperatures favor production of parent compounds (Blumer, 1976; Laflamme and Hites, 1978).

In summary, the amount and composition of PAHs emitted by a single source can vary greatly according to the combustion conditions and it is therefore extremely difficult to anticipate the assemblage and quantity of PAHs emitted.
knowing only the type of fuel (Colm-sjo et al., 1986; Jenkins et al., 1996; Ramdahl et al., 1982).

1.1.4. Physicochemical properties

PAHs range from slightly soluble in water (Naphthalene) to extremely insoluble (Dibenzo (a,h) Anthracene, DBA), and from volatile (Naphthalene) to semi-volatile (perylene; Table 1.1). Typically, the higher the mass of the compound, the lower its vapor pressure and water solubility. Because of the effect that mass has on these parameters, PAHs also show a decrease in vapor pressure and water solubility with increasing alkyl substitution (Boehm and Quinn, 1973; Garrett et al., 1998). The compounds are generally lipophilic, a property that increases with increasing complexity of the compounds (Harvey, 1997).

1.1.5. Environmental fate

1.1.5.1. Gas/particle partitioning

The environmental fate of PAHs is primarily controlled by their physicochemical properties, although natural processes (e.g., biological degradation), concentration of oxidizing pollutants (e.g., NO\textsubscript{x}, O\textsubscript{3}, OH\textsuperscript{+} radicals), temperature, light intensity, and type of sorbent are also important factors (Kamens et al., 1988; Matsuzawa et al., 2001). The principal mechanisms for removal of PAHs from the atmosphere are deposition and photo-chemical transformation. Both dry and wet deposition of gaseous and particulate PAHs may be important. Pyrogenic PAHs are emitted into the atmosphere either in the gas or particulate phases. The partitioning of different PAHs between gas and particle phases regulates the efficiency of removal from, and transport to, the atmosphere. Rain scavenging and dry deposition processes are highly dependent on the relative amounts present in the gas and particle phase. In addition, the size distribution of the particles is important for the efficiency of
### Table 1.1. Physical and chemical properties of PAHs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbr</th>
<th>Mol wt</th>
<th>Mol Formula</th>
<th>Melting Pt (°C)</th>
<th>Boiling Pt (°C)</th>
<th>Vap Press Pa at (25°C)</th>
<th>Log K_{ow}*</th>
<th>Water solubility at (25°C) μg/l</th>
<th>Henry's constant at (25°C) KPa m^3/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>Naph</td>
<td>128</td>
<td>C_{10}H_{12}</td>
<td>81</td>
<td>217.9</td>
<td>1.4</td>
<td>3.4</td>
<td>3.17 x 10^4</td>
<td>4.89 x 10^-2</td>
</tr>
<tr>
<td>Acynaphthylene</td>
<td>Acy</td>
<td>152</td>
<td>C_{10}H_{12}</td>
<td>92-93</td>
<td>265-275</td>
<td>8.8 x 10^-1</td>
<td>4.07</td>
<td>-</td>
<td>1.14 x 10^-3</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>Acen</td>
<td>154</td>
<td>C_{12}H_{10}</td>
<td>85</td>
<td>279</td>
<td>2.9 x 10^-1</td>
<td>3.92</td>
<td>3.93 x 10^3</td>
<td>1.48 x 10^-2</td>
</tr>
<tr>
<td>Fluorene</td>
<td>Flu</td>
<td>166</td>
<td>C_{13}H_{10}</td>
<td>115-116</td>
<td>293-295</td>
<td>8.0 x 10^-2</td>
<td>4.18</td>
<td>1.98 x 10^3</td>
<td>1.01 x 10^-2</td>
</tr>
<tr>
<td>Anthracene</td>
<td>Anth</td>
<td>178</td>
<td>C_{14}H_{10}</td>
<td>216.4</td>
<td>342</td>
<td>8.0 x 10^-4</td>
<td>4.5</td>
<td>73</td>
<td>7.3 x 10^-2</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>Phen</td>
<td>178</td>
<td>C_{14}H_{10}</td>
<td>100.5</td>
<td>340</td>
<td>1.6 x 10^-2</td>
<td>4.6</td>
<td>1.29 x 10^3</td>
<td>3.98 x 10^-3</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>Flan</td>
<td>202</td>
<td>C_{16}H_{10}</td>
<td>108.8</td>
<td>375</td>
<td>1.2 x 10^-3</td>
<td>5.22</td>
<td>260</td>
<td>6.5 x 10^-4</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Pyr</td>
<td>202</td>
<td>C_{16}H_{10}</td>
<td>150.4</td>
<td>393</td>
<td>6.0 x 10^-4</td>
<td>5.18</td>
<td>135</td>
<td>1.1 x 10^-3</td>
</tr>
<tr>
<td>Benz[a]Anthracene</td>
<td>B[a]A</td>
<td>228</td>
<td>C_{18}H_{12}</td>
<td>160.7</td>
<td>400</td>
<td>2.8 x 10^-5</td>
<td>5.16</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>Chrysene</td>
<td>Chry</td>
<td>228</td>
<td>C_{18}H_{12}</td>
<td>253.8</td>
<td>448</td>
<td>8.4 x 10^-5</td>
<td>5.91</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Benz[b]Fluoranthene</td>
<td>B[b]F</td>
<td>252</td>
<td>C_{20}H_{12}</td>
<td>168.3</td>
<td>481</td>
<td>6.7 x 10^-5</td>
<td>6.12</td>
<td>1.2</td>
<td>5.1 x 10^-5</td>
</tr>
<tr>
<td>Benz[k]Fluoranthene</td>
<td>B[k]F</td>
<td>252</td>
<td>C_{20}H_{12}</td>
<td>215.7</td>
<td>480</td>
<td>1.3 x 10^-8</td>
<td>6.84</td>
<td>2.5</td>
<td>4.4 x 10^-5</td>
</tr>
<tr>
<td>Benz[a]Pyrene</td>
<td>B[a]P</td>
<td>252</td>
<td>C_{20}H_{12}</td>
<td>178.1</td>
<td>496</td>
<td>7.3 x 10^-7</td>
<td>6.5</td>
<td>3.8</td>
<td>3.4 x 10^-5</td>
</tr>
<tr>
<td>Benz[ghi]Perylene</td>
<td>BgP</td>
<td>276</td>
<td>C_{22}H_{12}</td>
<td>278.3</td>
<td>545</td>
<td>1.4 x 10^-8</td>
<td>7.1</td>
<td>0.26</td>
<td>2.7 x 10^-5</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]Pyrene</td>
<td>IP</td>
<td>276</td>
<td>C_{22}H_{12}</td>
<td>163.6</td>
<td>536</td>
<td>1.3 x 10^-8</td>
<td>6.58</td>
<td>62</td>
<td>2.9 x 10^-5</td>
</tr>
<tr>
<td>Diben[z]h]Anthracene</td>
<td>DBA</td>
<td>278</td>
<td>C_{22}H_{12}</td>
<td>266.6</td>
<td>524</td>
<td>1.3 x 10^-8</td>
<td>6.5</td>
<td>0.5 (27°C)</td>
<td>7 x 10^-6</td>
</tr>
</tbody>
</table>

*n-octanol/water partition coefficient
wet and dry deposition. The partitioning of PAHs between gas and particle phases depends on the ambient temperature, relative humidity, the properties and the concentration of PAHs, and on the chemical composition of the aerosol particles (Goss and Schwarzenbach, 1998).

Semi empiric partitioning constants have been used to estimate the partitioning (Pankow, 1991). As a rule of thumb, Baek et al. (1991a) proposed that two- and three-ring PAHs are mainly in the gas phase, four ringed PAHs are in both gas phase and particle phase, and five- and six-ringed PAHs are mainly attached to particles.

1.1.5.2. Photo-degradation and chemical oxidation

PAHs present in the atmosphere are susceptible to both chemical oxidation and photochemical alterations (Baek et al., 1991b). PAHs can react with atmospheric ozone ($O_3$), NOx, SOx, and OH' radicals to form products sometimes more toxic than the PAH precursor, as in the case of nitro-PAHs.

Photochemical reactions also have important effects on the fate of PAHs. The degree to which a compound is susceptible to photolytic reactions is dictated, among other things, by its absorption spectrum and by the nature of the particle to which it is absorbed (Schwarzenbach et al., 2003). The difference in susceptibility to photodegradation can markedly change the relative proportion of these compounds during atmospheric transport (Gschwend and Hites, 1981). The association of PAHs with soot is thought to protect these compounds from transformations in the atmosphere.

1.2. PAHs in soil

Soils mainly comprising of mineral particles and organic matters, is a major reservoir and sink for urban pollutants because of their quantity and holding
capacity for pollutants (Wild and Jones, 1995). Soil is also a good indicator of pollution and environmental risks. It is continuously subject to pollution because of its open-system nature. Together with its capability to accumulate various pollutants, soil serves as a medium to integrate historical and recent pollution status indirectly. Fine soil particles, together with the adsorbed pollutants can enter human body via various pathways through direct ingestion and inhalation of the dust (Office of Emergency and Remedial Response, 1996) or indirectly from food in contaminated areas (Abdullah, 1995). In addition, toxic effects to soil organisms such as earthworms when in contact with PAH contaminated soils have been observed (Sverdrup et al., 2002).

PAHs have been detected around the world even at sites which are located far from industrial activity such as the Polar Regions, and in the tropics (Wania and Mackay, 1996). As the Arctic is far from all industrial sources, anthropogenic PAHs could only have reached it by long-range atmospheric transport (LRAT). According to the "Global Distillation" hypothesis of Wania and Mackay (1996) this should result in a fractionation of the PAH pattern according to the volatility of the individual compounds. The compounds (POPs) with certain physicochemical properties are susceptible to long-range atmospheric transport (Whylie et al., 2003). LMW PAHs are subject to transport to remote areas and considered as "multi-hop" chemicals, while HMW PAHs associated with particles undergo "single hop" transport behavior, which are prone to rapid deposition and retention close to the source region. So, due to their various transport potential, PAHs may become fractionated during the transport through the atmosphere, and it would be observable as a changing mixture of compounds along the route from source to sink. Besides the global fractionation by long-range
transport, a PAH fractionation can also occur at the local scale along short-distance transects from point emitters of PAHs (Wilcke et al., 1996; Meharg et al., 1998). Thus, atmospheric transport of PAHs changes the PAH composition and might be one control of systematic differences in soil PAH patterns across different climatic zones.

The typical level of endogenous total PAHs in soils is in the range 1-10 µg kg\(^{-1}\) resulting from plant synthesis and natural fires (Edwards, 1983). As anthropogenic activities are the main sources of PAHs, the levels of PAHs in soils in urban areas are approximately a factor of 2–10 higher than those in rural areas (Lodovici et al., 1994; Wagrowski and Hites, 1997). Although most of the emitted PAHs are dispersed, a part remains in the vicinity of the source (Hewitt and Rashed, 1990). Urban areas with high population densities show high PAH concentrations, which are mainly caused by traffic emissions (Pfeffer, 1994). On the other hand, compartments in rural regions are generally less contaminated (Jones et al., 1989\(^a\)), with the exception of compartments in the direct vicinity of large PAH sources.

**1.2.1. Sources of PAHs in soil**

PAH in soils can arise from a number of sources. Point sources include incomplete combustion of fossil fuels e.g. wood burning (Freeman and Catteil, 1990), hydrocarbon spillage (Benner Jr. et al., 1990), use of organic waste as compost and fertilizer (Smith et al., 2001), power plants and blast furnaces (Van Brummelen et al., 1996). However, the major pollution is likely to be from diffuse sources such as deposition from the atmosphere and there is evidence to indicate that PAHs are transported over long distances by atmospheric movement (Lunde and Bjorseth, 1977; Aamot et al., 1996; Halsall et al., 2001).
In recent literature, there are strong indications that three PAHs namely, naphthalene, phenanthrene, and perylene are produced biologically; in addition to their presence in the exhaust fume of combustion processes. Naphthalene and phenanthrene also occur in spills of unburnt petroleum (Aislabie et al., 1999). There were early indications that phenanthrene can be produced biologically from alkylphenanthrene precursors in plant debris (Sims and Overcash, 1983). Furthermore, it is known that perylene is produced biologically in anaerobic environments in soils and sediments (Venkatesan, 1988; Guggenberger et al., 1996; Wilcke et al., 2002).

1.2.2. Fate in soil

Fate of PAHs in soil is governed by many processes (Figure 1.1, Figure 1.2) e.g. sorption/desorption, leaching, volatilization, chemical and biological degradation etc. Soil organic matter holds PAHs strongly and overweighs the loss mechanisms. This leads to their accumulation in soil matrix.

1.2.3. PAH-TOC (total organic carbon) relationship

PAHs are strongly retained by the soil matrix. However, the nature of the association of PAHs with soil particles remains unresolved. Various mechanisms have been proposed, including partitioning, surface adsorption, intraparticle transport and trapping within the interior of aggregates (Chiou et al., 1979; Karickhoff and Brown, 1979; Readman et al., 1987). The partitioning concept of soil sorption implies that the sorption of hydrophobic organic molecules is determined by the organic carbon content of the substrate (Karickhoff and Brown, 1979; Means et al., 1980). It is commonly observed that PAH concentrations in soils are affected by organic carbon content (TOC) of soils, with higher concentrations accompanied with high TOC (Wilcke, 2000; Wilcke and Amelung,
2000; Tam et al., 2001; Ribes et al., 2003). However, ionic strength (Lee et al., 2003), pH (Laor et al., 1998) and colloids may also influence the binding of PAHs in soils.

Figure 1.1. Processes involved in the exchange of SVOC across the soil-air interface: Air-soil interface Review (Adopted from Cousins et al., 1999).

1.2.4. Losses of PAHs from the terrestrial environment

It is important to emphasize that the environment is a dynamic system through which chemicals such as PAHs are produced, transported, deposited and
transformed. Thus, PAHs once incorporated into terrestrial compartments are not static and recalcitrant. Losses of PAHs can be via several processes; the major mechanisms include biodegradation, chemical transformation, photolysis, volatilization, leaching, metabolism and erosion.

Figure 1.2. The diagram depicts relation of partition coefficients describing POP partitioning between main soil components and respective physical-chemical properties of the chemicals given in brackets (Adopted from Vassilyeva and Shatalov, 2002).

Erosion is often disregarded as a loss mechanism. Metabolism by higher animals is the mechanism by which PAHs exhibit their carcinogenic potential. Leaching of PAHs from soil surface horizons to deeper aquifers may be viewed as a loss mechanism. However, most PAHs are either too well adsorbed on to soil...
organic matter or degradable that total leaching losses are not expected to be an important loss mechanism. Leaching of PAHs may be more significant where there is ground contamination with solvents. PAH susceptibility to degradation is now well characterized as being structure dependent. Several studies have revealed that degradation potential decreases as the number of benzene rings in the PAH molecule increases (Sims & Overcash, 1983; Park et al., 1990; Wild & Jones, 1993). PAH degradation is also dependent on other factors such as previous contamination of the soil with PAHs, sludge application, soil structure, environmental conditions, presence of vegetation, etc. However, there is evidence to show that the HMW PAHs exhibit a higher propensity for long-term enrichment in agricultural soils than LMW compounds, due to their greater resistance to degradation and volatilization (Jones et al., 1989a). PAHs may also be lost by biodegradation and chemical transformations in water and sediments, while processes such as photolysis may be an important loss mechanism for some compounds in watercourses (Sanders et al., 1993). Soil-to-air recycling of PAHs is a potentially important, but poorly understood flux mechanism. Volatilization may be an important pathway of PAH loss especially for LMW compounds. Volatilization is influenced by several physicochemical (Henry’s constant) and environmental factors (wind speed, atmospheric turbulence and temperature). Volatility (expressed as Henry’s constants) decreases as molecular weight increases (Sims and Overcash, 1983).

1.3. PAH Exposure in Humans

Humans can be exposed to PAHs a) through the respiratory tract by inhalation of PAH-containing matters such as cigarette smoke, vehicle exhaust, PAH contaminated air emitted from certain industries or by the burning of wood for
heating, etc., b) through the digestive tract following intake of PAH-containing foodstuffs (e.g., fried and charcoal-grilled meat) and PAH contaminated vegetables and crops grown close to areas with intense traffic, etc., c) direct contact with polluted soils and d) through the skin following contact with substances such as petroleum products (e.g., soot, pitch, and tars). Several organs are believed to be susceptible to tumor formation after exposure to PAHs (Doll et al. 1994; IARC 1983, 1987a, b; U.S. PHS 1979). These include the lungs (in particular the bronchi), the skin, the esophagus and colon, the pancreas, the bladder, and the breast in women.

Accumulation of PAHs in soils may lead to contamination of vegetables and food chains (Kipopoulou et al., 1999), leading to direct or indirect human exposure. Studies have found that the amount of human exposure to PAHs through soils was higher than through air or water (Menzie et al., 1992). Some other studies have also shown that the intake of PAHs via the diet is large (Beckman et al., 1998; de Vos et al., 1990) and much higher than the intake via inhalation (Lioy et al., 1988; Lodovici et al., 1995; Vaessen et al., 1988; WHO/IPCS, 1998). Data on the origin of PAHs in food are limited; however, it has been suggested that the major part originates from precipitated particulate material (de Vos et al., 1990; Lodovici et al., 1995). In fact, it has been demonstrated that the PAH content is higher in products from crops cultivated near roads and cities (Larsson, 1986).

1.3.1. Comparative cancer potency of individual PAH compounds relative to B(a)P

Many PAH compounds are classified by the IARC as probable or possible human carcinogens, and several authors have used data from various cancer tests to rank
Table 1.2. Relative potency of individual PAHs compared with B[a]P (TEF values), according to different authors

<table>
<thead>
<tr>
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<td>Anth</td>
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<td>0.0005</td>
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<tr>
<td>Phen</td>
<td>0.001</td>
<td>0.014</td>
<td>0.1</td>
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<td>0.005</td>
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<td>B[a]A</td>
<td>0.013</td>
<td>0.145</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Chry</td>
<td>0.001</td>
<td>0.0044</td>
<td>0.1</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Flan</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Pyr</td>
<td>0.081</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>B[a]P</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B[b]F</td>
<td>0.08</td>
<td>0.14</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>B[k]F</td>
<td>0.04</td>
<td>0.066</td>
<td>0.1</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>DBA</td>
<td>0.69</td>
<td>1.11</td>
<td>5</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>BgP</td>
<td>0.022</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>IP</td>
<td>0.017</td>
<td>0.232</td>
<td>0.1</td>
<td>0.1</td>
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</tr>
</tbody>
</table>

(Adopted from Bostrom et al., 2002)
the compounds according to cancer potency relative to B[a]P. Although such comparative rankings are not based on inhalation experiments but on other cancer tests, the results may still be used for grouping of individual PAH compounds as more or less potent. Toxic equivalency factors (TEFs) can be used as a practical tool for regulatory purposes for large groups of compounds with a common mechanism of action (e.g., dioxin like compounds and PAHs) when there are limited data except for one reference compound, 2,3,7,8-tetrachlorodibenzo-p-dioxin and B[a]P, respectively.

Several authors have calculated the relative potency of different PAHs compared with the potency of B[a]P in bioassays such as the skin application tumor assay in mice, or other cancer tests. Recently, Nisbet and LaGoy completed a new list of TEFs which seems to better reflect the actual state of knowledge on the relative potency of individual PAHs (Nisbet and LaGoy, 1992). The TEF value of B[a]P is set as 1. In almost all of the published rankings Table 1.2, the TEF value for most of the other PAHs is less than 1, except for dibenz[a,h]anthracene, which was given TEF values higher than 1 by some authors. Phenanthrene, pyrene, anthracene, and fluoranthene, which occur at relatively high concentrations in ambient air but are generally not considered to be carcinogenic, have been assigned low but varying TEF values by some authors but not by others. However, fluoranthene is an experimental carcinogen in a specific test system, and in a recent TEF scheme, fluoranthene was assigned a higher TEF value (0.05) (Larsen and Larsen 1998).

1.4. Study area

Delhi, the National Capital Territory of India, has a geographic area of 1,483 sq km stretched in east west width approximately 51.9 km and northwest width approximately 48.48 km. Delhi is located 160 km south of Himalayas at a latitude of 28°24'17" to 28°53' N and longitude 76°20"37"to 77°20'37" E with an average
altitude 216 meter above sea level. To the west of Delhi is the Indian Desert (Thar Desert) of Rajasthan. In the south, the central hot plateau and the cooler hilly region to the north and east.

The physiography of Delhi comprises of almost flat plain land with a cluster of sand dunes on the south western part and a long rocky ridge extending roughly from the north north east to south south east. Due to its abundant trees and plant life, the ridge is often called as the lung of Delhi. The river Yamuna which enters from the north eastern edge passes through the Shahdara Block and marks the south eastern boundary of the territory. Thus physiographically, 3 segments make the Delhi territory: i) the Yamuna flood plain ii) the basin area, west of the flood plain, called Dabar iii) the rocky outcrop of Aravalli called Kohi. The shape of the city can be said as circular with radial patterns. The population of the state is 13.78 million with a density of 9,294 persons per sq. km (2001 census). Urban population is 93% and rural population 7%. Total livestock population is 0.32 million (1992 livestock census).

1.4.1. Climate

The climate of Delhi is mainly influenced by its inland position and the prevalence of continental air during the major part of the year. Extreme dryness with an intensively hot summer and cold winter are the main characteristics of the climate. The normal rainfall in Delhi is 611.8 mm. About 81% of the annual rainfall is received during the monsoon months. January is the coldest month with the mean daily maximum temperature at 21.3 °C and mean daily minimum at 7.3 °C. May and June are the hottest months with temperatures touching 46-47 °C. The average annual temperature ranges between 22 °C to 25 °C. Except during the monsoon months, winds are predominantly from a westerly or north westerly direction and tend to be more
northerly in the afternoon. Easterly and south easterly winds are more common in the monsoon months.

1.4.2. Land use pattern

Land use in the National Capital Territory (NCT) of Delhi during the last two decades has undergone significant changes due to pressure of floating and ever increasing population, rapid industrialization and urbanization and demand of agricultural produce vital for the urban areas. The potential agricultural land has been reduced by 60% within 25 years due to urban, infrastructural and industrial demand for land in and around the NCT. Out of the total geographical area of 1483 sq km about 151 sq km constitutes the forest & tree cover. Of this 111 sq km has been classified as forest cover and the rest as tree cover outside the forest area like village wood lots, block plantations, road side, pond side, railway side, canal side and others. (http://forest.delhigovt.nic.in/delhi_state.html). The area under forest is small and decreasing because of deforestation for land, fuel and other domestic uses. About 14.4% of NCT land area is chemically degraded (Sehgal and Abrol, 1994). Peri-urban lands of New Delhi are intensively cultivated with vegetable crops (Singh and Kumar, 2006).

1.4.3. Major activities contributing to the environmental pollution

Delhi figures conspicuously in the world pollution map for the simple reason that it is one of the most polluted cities in the world. Delhi is termed as the fourth most polluted city in the world. This dubious distinction was with reference to the higher particulate levels in Delhi atmosphere.

Increasing industries have been the major cause of concern due to the increasing pollution problems in the city. As per a survey conducted by the NPC in 1996, there are total 1,26,218 registered industrial units in 28 authorized industrial
estates and several nonconforming areas. Nearly two third of all industrial units are located in six larger industrial areas namely Anad Parbat (17.23%), Mayapuri (15.10%), Okhla (9.59%), Wazirpur (7.70%) and Kirtinagar Industrial Areas (6.82%). Only one third of the units are located in the remaining 22 industrial areas. There are 3 power plants namely Badarpur (720MW), Indraprasta (277MW coal based and 180MW gas based) and Rajghat (135MW). In addition, Shriram food and fertiliser industry also has a captive power unit of 32MW. Vehicular emissions out rank even sources of pollution like thermal power plants, industries and domestic coal burning and account for as much as 65% of the total pollution load in Delhi. Thermal power plants rank second with 16%, industry 12%, followed by the domestic sector at 7%. The vehicular population has increased phenomenally, from 2.35 lakhs in 1975 to 51.4 lakhs in March 2007, and expected to touch 60 lakhs in 2011.

1.4.4. Pollution status of the Yamuna River

River Yamuna, a tributary of River Ganga, flows in a stretch of 1376 km from Yamunotri to Allahabad. It is one of the most polluted rivers of India and is affected during its course by three major urban centers viz; Delhi, Mathura-Vrindavan and Agra. Among these three urban centers, Delhi has been a major contributor in terms of pollution load to the river Yamuna. Yamuna River traverses around 22 km through the union territory of Delhi. As it flows through Delhi, it receives large quantities (3000 MLD) of partially treated and untreated industrial and domestic sewage through twenty-two major drains. The total calculated discharge of these 22 drains is approx. 46.30m3/s, which contributes 311.05 tonnes of BOD load per day. From the total discharge of these drains Yamuna receives more than 90% (http://www.cpcb.nic.in/ar2002/ar1-2ch5.htm). This turns the river into a deadly concoction of disease-bearing water for the poor people living downstream, as
Yamuna is the main source of drinking water for them. Some 3.5 lakh people live in slum houses that have come up on the Yamuna riverbed and its embankments. Though effluent from various drains is accounted for the maximum, fly ash dumps from two major power plants and wastes from riverside slum houses also contribute to the pollution load of the river.

The contamination of floodplain soils has recently begun to attract growing attention; previously, interest was mainly focused on river water, sediments, and various types of aquatic animals (Franke et al., 1995; Heininger et al., 1998). Yet, while polluted rivers slowly become cleaner once the source of pollution has been removed, floodplain contamination persists for much longer because contaminated sediments, once deposited in a floodplain are not removed easily after they have been covered by vegetation. Floodplains can be regarded as a huge depot of anthropogenic pollutants (Witter et al., 2003).

1.5. Significance of the study

The environmental pollution by PAH is not a problem of a single country, but a worldwide problem, due to the variability and distribution of the PAH sources and their long-range transport. In developed countries enough data is available on PAH levels in soil, but in India, such studies are rare. However there are few studies, which quote levels of PAHs in other environmental compartments, like air, sediment etc. According to these studies PAH levels in Indian cities like Delhi lies on the higher side of pollution spectrum. As PAH concentrations in air can be well correlated with levels of PAHs in soils, we can expect that Delhi soils might also be contaminated with PAHs. Thus, Delhi region was considered as a potential area for such investigation.
1.6. Objectives

In Delhi, considering the rapid growth in vehicular population, urbanisation and the industrial activities on one hand and the lack of studies pertaining to their environmental and health repercussion on the other hand, such studies are considered to be of paramount importance.

The study was therefore planned with the following objectives:

i. To determine the PAH contamination level in the surface soils of Delhi region with different land use patterns.

ii. To investigate the spatial distribution and seasonal variation of 16 priority PAH compounds in the surface soils of Delhi region.

iii. To determine the organic carbon content of soils.

iv. To examine the relationship between PAH concentrations and soil properties, mainly total organic carbon content.

v. To study source apportionment by isomer pair ratios and principal component analysis (PCA) in order to determine the predominant sources of PAHs in the study area.