



*Chapter 1*

**INTRODUCTION**

**Environmental pollution** is one of the major issues facing the world today. Rapid growth of industries, population and traffic density, over the past few decades emerged as a serious determinant of environmental quality for air, water and soil. This is of particular concern in the developing countries. Environmental pollution is closely related to economic growth, as economic growth is necessary to fulfill consumers demand for goods but it is unavoidably accompanied by pollution [1]. Release of hazardous pollutants into the environment degrades the environmental quality as well as has a negative impact on human health [2].

The oil and petroleum industry is the most significant and promising sector of modern civilization. Rapid development of this industry with increasing demand for oil during the last few decades has triggered air, water and soil pollution [3, 4]. Moreover, areas surrounding oil industries have become contaminated due to the activities, such as oil exploration and production, refining and petro-chemistry which release various organic and inorganic pollutants into the soil, air and water including heavy metals, Total Petroleum Hydrocarbons (TPH) and Polycyclic Aromatic Hydrocarbons (PAHs) and pollute the environment [5]. PAHs also can be released from the major oil spillages or minor leakages of petrol from fuel storage tanks and pipelines, mechanical workshops and petrol stations [6, 7]. Crude and refined oil contains substantial amounts of PAHs, arising from chemical transformation of natural product molecules, such as steroids to aromatic hydrocarbons [8]. Crude oil mining had become the main pollutant source of PAHs in soil and groundwater [9]. The presence of heavy metals such as vanadium, copper, nickel, cobalt, and chromium in crude oil has also been reported [10,11].

### **1.1 Polycyclic Aromatic Hydrocarbon (PAHs)**

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of ubiquitous, semi volatile organic pollutants consisting of two or more fused aromatic rings made up of carbon and hydrogen atoms. PAHs are considered as hazardous air pollutants (HAP) in the group of the non-halogenated organic compounds along with benzene, phenol, aldehyde [12]. Due to their stable chemical structure and low bioavailable fraction PAHs are moderately persistent compounds in the environment [13]. Depending on the molecular structure, PAHs are classified into two major categories viz. low

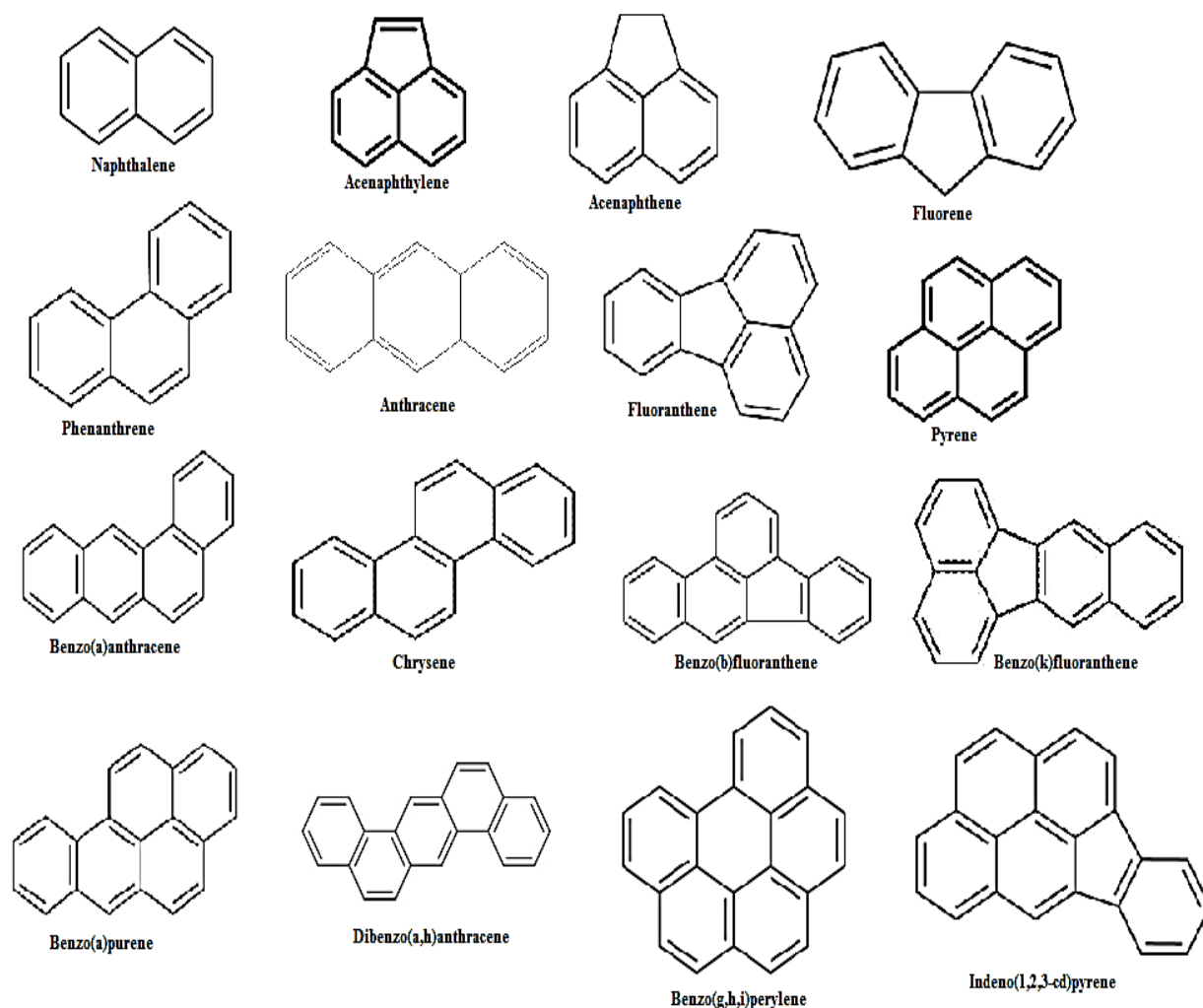
molecular weight (LMW) PAHs (2-, 3- and 4-ring) and high molecular weight (HMW) PAHs (5-, 6-ring) [14, 15]. The LMWPAHs include Naphthalene (Nap), Acenaphthylene (Any), Acenaphthene (Ane), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr) and the HMWPAHs include Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Dibenzo[a,h]anthracene (DaA) Benzo(g,h,i)perylene (BgP) and Indeno[123-c,d]pyrene (IcdP). The United States Environmental Protection Agency (USEPA) and the European Union (EU) have reported 16 PAHs as priority pollutants (name of 16 PAHs with their abbreviation is given in table 1.1) [16, 17], which are targeted as measurement for environmental pollution in different matrices. Out of these 16 PAHs, seven PAHs namely, BaA, Chr, BbF, BkF, BaP, DaA and IcdP has classified as Group B2, probable human carcinogens by the USEPA [18]. Considerable ecotoxicological concern has been attracted by these compounds due to their low aqueous solubility, semi-volatility, high octanol–water partition coefficient ( $K_{ow}$ ) and their potential carcinogenicity [19].

### 1.2 Structure of PAHs

The PAHs constitute a wide range of compounds consists of carbon and hydrogen atom arranged in the form of fused benzene rings (linear, cluster or angular arrangement) [20]. They don't contain any hetero atom or carry substituent. The molecular structure of 16 PAHs are shown in fig. 1.1.

### 1.3 Physico-chemical properties of PAHs

The PAHs are neutral, non-polar hydrophobic organic compounds which are weakly soluble in water. Their aqueous solubility decreases with increasing the number of aromatic rings or with increasing molecular weight. They are lipophilic in nature and mostly soluble in organic solvents, which also facilitated them to accumulate in animal tissues [21]. At a temperature of 18-20<sup>0</sup>C PAHs are solid, colorless or white or



**Fig. 1.1 Molecular structures of 16 USEPA priority PAHs.**

light yellow-greenish colored [22]. In general all the PAHs are solid with high melting and boiling points and low vapour pressure. They are also highly sensitive to temperature and light [23]. They degrade at high temperature (50<sup>0</sup>C) and at exposure to ultraviolet and visible lights. The PAHs with same number of rings but difference in configuration may lead to difference in their properties. Table 1.1 presents the physico-chemical properties of 16 PAHs. They hold very characteristic UV absorbance spectra, and each PAH ring structure has a distinctive UV spectrum, thus each isomer has a different UV absorbance spectrum.

The PAHs are resistant to degradation and can persist in the environment, thus are potential pollutants to cause adverse effect to the environment [24]. Substituted PAHs

with functional groups such as  $-\text{OH}$ ,  $-\text{NO}_2$ ,  $=\text{O}$  and  $-\text{CH}_3$  are also present in the environment and they are more reactive in the environment.

### 1.4 Sources of PAHs in the environment

The PAHs originate from both natural as well as anthropogenic sources along with some minor biogenic sources. Natural sources of PAHs include forest fires, volcanic eruption. But the predominant sources of PAHs are anthropogenic. The anthropogenic sources of PAHs can be categorized into two groups: pyrogenic and petrogenic. Petrogenic PAHs are originates from petroleum including crude oil, lubricants and their derivatives. Petrogenic PAHs are introduced into the aquatic environment through accidental oil spills, discharge from routine tanker operations, municipal and urban runoff [25]. Petroleum is a complex mixture of different organic compounds formed during different geological ages and under different geological conditions. The different depositional environments during oil formation are reflected in different PAH distributions in crudes from different sources. The main PAHs components of a petroleum source include the EPA 16 parent PAHs and the petroleum-specific alkylated homologues of selected PAHs: viz., alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene series, which are also called “the alkylated five” or “five target” [26]. Pyrogenic PAHs are produced from oxygen depleted, high-temperature combustion of fossil fuels and biomass (e.g., incomplete combustion, pyrolysis, cracking, and destructive distillation). In pyrogenic PAH patterns, unsubstituted compounds predominate over their alkylated homologues. Petroleum derived PAHs are preferred as biodegradable in comparison to combustion derived ones [27].

The anthropogenic sources of PAHs can also be classified as mobile and stationary sources. Mobile sources include the vehicular emission from the burning of diesel or gasoline driven vehicles. On the other hand stationary sources include combustion activities in residential (furnaces, fireplaces and stoves) as well as industrial operations (mainly coke and carbon production, petroleum processing, aluminum sintering) [28].

Biomass burning, including both biofuel combustion and wildfires is considered as the dominating source of PAHs emission contributing 56.7 and 17.0% of the total global PAHs emissions, respectively. Almost 50% of the global PAHs emissions were naphthalene (Nap) and another 38% were LMWPAHs including 3-4 ring compounds. In contrast, HMWPAHs, with 5–6 rings, accounted for only 2.4% of the global PAHs emission [29].

### 1.5 Toxicity of PAHs

The PAHs represent a group of toxicological compounds which generates a variety of hazardous effects including genotoxicity, immunotoxicity, developmental toxicity, reproductive toxicity and carcinogenicity [30, 31]. High PAHs concentrations in the environment cause various adverse effects on different types of organisms like plants, birds and mammals including both acute and chronic toxicity. The LMWPAHs (apart from Nap) are generally associated with relatively lower toxicity (cancer risk) compared to HMWPAHs with more than 5 aromatic rings [32]. BaP is considered as the most toxic PAH or index for the whole group of PAHs due to its high carcinogenic potency. The toxicity of PAHs compounds is calculated as toxicity equivalency factor (TEF) for each PAH, which is an estimate of the relative toxicity of the PAH compound compared to BaP and expressed as BaP<sub>eq</sub> concentration (BaP equivalent).

The PAHs enter into the body through food and water intake or skin contact. Though high level of PAHs is not generally detected in raw foods, grilled foods have been reported to contain PAHs at levels varying from 0 to 130 mg kg<sup>-1</sup>. Apart from analytical difference, this variation in PAHs levels in foods is mainly due to the type and fat content of the food, cooking process (fried, grilled, roasted, boiled and smoked), temperature and duration of cooking, type of fuel used (electrical, gas, wood, and charcoal) and proximity and direct contact with heat source [33]. Human exposure to PAHs has been allied with an augmented risk of developing cancer in variety of organs (such as lung, bladder, stomach, skin, larynx, scrotum, breast, oesophagus, prostate, kidney and pancreas). Moreover, they are responsible to suppress the immune system and are suspected of being endocrine disrupters [34, 35].

Table 1.1 Physico-chemical properties of 16 USEPA priority PAHs [36].

Names of PAHs	Abbreviation	Molar mass (g/mol)	Molecular Formula	No. of Rings	Boiling Point (°C)	Melting Point (°C)	Solubility in water (mg/l)	log p (octanol-water partition coefficient)	Vapour Pressure kPa
Naphthalene	Nap	128	C <sub>10</sub> H <sub>8</sub>	2	218	80.26	3.93	3.30	1.1×10 <sup>-2</sup>
Acenaphthylene	Any	152	C <sub>12</sub> H <sub>8</sub>	3	280	91.8	3.93	3.94	3.9×10 <sup>-3</sup>
Acenaphthene	Ane	154	C <sub>12</sub> H <sub>10</sub>	3	279	93.4	1.93	3.92	2.1×10 <sup>-3</sup>
Fluorene	Flu	166	C <sub>13</sub> H <sub>10</sub>	3	295	116-117	1.68-1.98	4.18	8.7×10 <sup>-5</sup>
Phenanthrene	Phe	178	C <sub>14</sub> H <sub>10</sub>	3	340	99	1.2	4.46	2.3×10 <sup>-5</sup>
Anthracene	Ant	178	C <sub>14</sub> H <sub>10</sub>	3	340	218	0.076	4.45	36×10 <sup>-6</sup>
Fluoranthene	Fla	202	C <sub>16</sub> H <sub>10</sub>	4	375	110.8	0.2-2.6	5.16	6.5×10 <sup>-7</sup>
Pyrene	Pyr	202	C <sub>16</sub> H <sub>10</sub>	4	404	145-148	0.077	4.88	3.1×10 <sup>-6</sup>
Benzo(a)anthracene	BaA	228	C <sub>18</sub> H <sub>12</sub>	4	438	158	0.01	5.76	1.5×10 <sup>-8</sup>
Chrysene	Chr	228	C <sub>18</sub> H <sub>12</sub>	4	448	254	0.0028	5.50	5.7×10 <sup>-10</sup>
Benzo(b)fluoranthene	BbF	252	C <sub>20</sub> H <sub>12</sub>	5	481	168	0.0012	5.78	6.7×10 <sup>-8</sup>
Benzo(k)fluoranthene	BkF	252	C <sub>20</sub> H <sub>12</sub>	5	480	217	0.00076	6.11	2.1×10 <sup>-8</sup>
Benzo(a)pyrene	BaP	252	C <sub>20</sub> H <sub>12</sub>	5	495	179	0.0023	5.97	7.3×10 <sup>-10</sup>
Dibenz(a,h)anthracene	DaA	278	C <sub>22</sub> H <sub>14</sub>	5	524	262	0.0005	6.75	1.3×10 <sup>-11</sup>
Benzo(g,h,i)perylene	BgP	276	C <sub>22</sub> H <sub>12</sub>	6	500	278	0.00026	6.63	1.3×10 <sup>-11</sup>
Indeno(1,2,3-c,d)pyrene	IcdP	276	C <sub>22</sub> H <sub>12</sub>	6	536	163	0.062	6.70	ca.10 <sup>-11</sup>

The most common mechanism of carcinogenesis made by PAHs is DNA damage through the formation of adducts, which alter the DNA sequence in genes that regulate cell replication results cancer [37]. Mutagenic PAHs, like BaP, generally have four or more aromatic rings as well as a "bay region", a structural pocket that increases reactivity of the molecule to the metabolizing enzymes. These metabolites can bind to DNA at specific sites, forming DNA adducts that can be stable or unstable. Stable adducts may lead to DNA replication errors, while unstable adducts react with the DNA strand, removing a purine base (either adenine or guanine). Such mutations, if they are not repaired, can transform genes encoding for normal cell signaling proteins into cancer-causing oncogenes. According to a recent directive of the European Commission [38], BaP is used as a marker for the carcinogenic risk of PAHs and establish a limit value for that substance, to be reached as far as possible 1 ng m<sup>3</sup>.

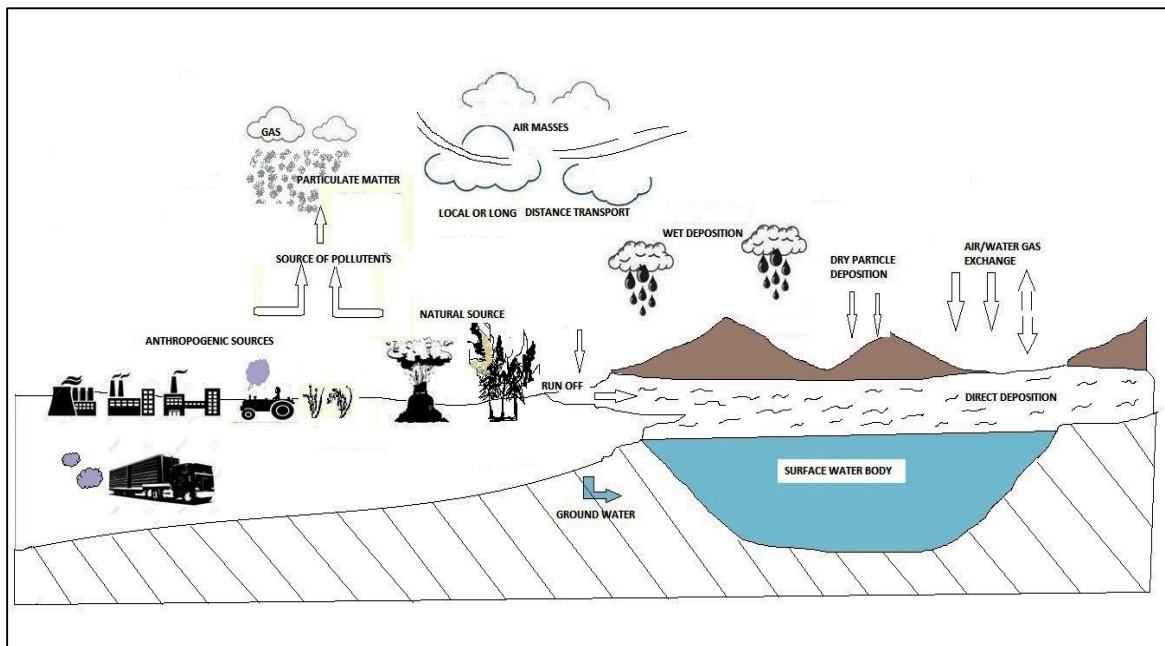
### **1.6 PAHs in different environmental matrices**

Recent researches have documented high accumulation of PAHs concentrations in soil, sediment, aquatic and atmospheric environments [17, 39, 40, 41, 42]. Furthermore, depending on the geographical location, the type of emission sources and the prevailing atmospheric characteristics, PAHs profile varies from one location to another. PAHs are included in the Convention for Long-Range Transboundary Air Pollution's (CLRTAP's) Persistent Organic Pollutants (POP) protocol: 1 as it has an ability to get transported to long distances and accumulate in remote and pristine areas [43].

Aerial movement is considered as the key pathway for environmental dispersal and transboundary deposition of PAHs [44]. Moreover, air–water and air–soil exchange processes, re-volatilization and atmospheric transformations are the significant mechanisms of controlling the fate of these compounds in the environment [45]. Atmospheric deposition is a major source of PAHs in soil and subsequently it moved to other compartments like water and sediment. Moreover sorption-desorption processes are the main controlling factor for distribution of PAHs in the soil and water



systems [46]. Fig. 1.2 depicts the distribution and transfer of PAHs in various environmental matrices.



**Fig. 1.2 Distribution and transfer of PAHs in various environmental matrices (Modified, USEPA [47])**

### ***1.6.1 PAHs in the atmosphere***

The PAHs enter into atmosphere mainly via combustion and volatilization processes [48]. Once released to the atmosphere, the fate of the gaseous PAHs mixtures depends upon their weight. Heavier PAHs ( $>$  four rings) have a tendency to associated with particulate matter, whereas lighter PAHs ( $\leq$  four rings) tend to remain in gaseous phase until removed via precipitation [23]. Various factors that affect gas-particle partitioning include ambient temperature, relative humidity, vapor pressure of PAHs, particulate matter, chemical composition and surface characteristics [49]. Both gas and particulate phase PAHs undergo various transformation reactions in the atmosphere. Among the gas-phase reactions, the most significant are reaction with  $-OH$  during daytime and with  $NO_3$  during the night time. Reaction of PAHs with ozone and photolysis act as a secondary process in transformation of gaseous PAHs. The gas-phase PAHs usually have shorter atmospheric lifetime than those found on particulate, since particulate phase processes are slower than the gas phase processes

[50]. PAHs compounds also sorbed onto inhalable particulate matter like PM<sub>2.5</sub> or PM<sub>10</sub>, which are considered to play a key role in causing adverse health effect [51]. Several toxicological studies in animals and occupational studies in humans determine an excess risk of lung cancer associated with PAH inhalation [52]. The residence time of PAHs in the atmosphere mainly governs by the particulate size and atmospheric conditions, small particles (~1 µm diameter) may be resides for few weeks, whereas, particles with a diameter of 1–10 µm for few days only [53]. PAHs are transported during long distances and become deposited in terrestrial and aquatic systems through wet and dry deposition [54]. Therefore, atmospheric transport and deposition constitute the primary pathway for distribution of PAHs from a variety of emission sources [55]

### ***1.6.2 PAHs in the Soil***

The PAHs released into the atmosphere in both particulate and gaseous phase are transported through the atmosphere and are ultimately deposited onto the soil. Atmospheric deposition (both dry and wet) is the most common and primary input of PAHs pollution in soil [20, 23, 56]. The combustion related PAHs travel far distance through long range atmospheric transport. On the other hand, crude or refined oil and petroleum, leakage from crude oil storage tanks, unburned fuel from vehicles contain significant quantity of PAHs which is the main petrogenic input of PAHs in soil [57]. Hence, soil is considered as the primary reservoir of PAHs accumulation in the environment and a good indicator of pollution status [58].

In the suburban areas, soil mostly used as agricultural fields, are liable to be polluted by PAHs generated and transferred from cities and thus have a great influence on food chain and human health. Consequently, PAHs pollution in soils of sub-urban areas has significantly risen up concern of many researchers [59].

Soil has a vital role in fate, transport and behavior of PAHs. According to Smith et al. [60] PAHs burden in the environment is mostly due to their presence in soil (approximately 95%), in contrast to air (approximately 0.2%). Combustion derived PAHs are mostly present in the topmost layer of soil [61]. Various studies reported that PAHs concentrations in soil were considerably related with the equivalent levels in air [62], house dust [63], urban street dust [64, 65] and plants [66]. From

contaminated soil, PAHs dispersed through various pathways like volatilization, irreversible sorption, leaching, accumulation by plants and biodegradation [67]. According to Menzie et al. [68] PAHs exposure to human through soil is higher in comparison with air or water.

Soil organic matter holds PAHs strongly and reduces the loss mechanisms [58] and thus they sustain in soil matrix for longer time. Sorption of PAHs in soil depends upon various properties like octanol/water partition co-efficient, aqueous solubility, vapour pressure, molecular size, chemical reactivity, soil pH, soil organic matter content, clay content and their type, moisture and temperature status. The persistency of PAH compounds in the environmental depends upon the PAH molecule size. For example, reported half-lives of the three-ring phenanthrene molecule may range from 16 to 126 days while for the five-ring molecule BaP they may range from 229 to >1,400 days in soil [69]. The PAHs content of soil is inversely proportional to the soil depth. The land use pattern also influences the concentration and distribution of PAHs in soil surface. The PAH-soil system is therefore regarded as high information content. As such, crude or refined oil and petroleum contain substantial amount of PAHs and therefore, the oilfield soils are useful indicators of the level and distribution of PAHs [57].

### ***1.6.3 PAHs in groundwater***

Atmospheric deposition has been considered as a chief path-way of PAHs to enter into water bodies [70]. The primary sources of PAHs contamination in groundwater may be seepages from waste disposal sites, oil spills, surface and underground storage tank leakages, agro-activities, effluents discharges and deliberate dumping [71]. Upon entering an aquatic system, due to their nature of hydrophobicity and high partition coefficients, PAHs tend to reside or partition onto the non-aqueous phase such as soil, sediment or adhered to the suspended particles [72, 73] and form a long term source of pollution. Thus adsorption is very important process in determining their transport to subsurface system [74]. The mobile colloids like clay particles are mainly associated in transporting these organic pollutants to a greater depth. Colloids, including both organic and inorganic, have a great ability in transporting metals, radionuclides and also the hydrophobic organic pollutants including PAHs. This ‘colloid facilitated transport’ is characterized as ‘the third phase of transport’ of these

pollutants into groundwater [75]. Contaminated groundwater sources pose possible threat to the local water consumers as well as the natural environment [76]. It has been also reported that PAHs concentrations in near surface groundwater may increase after periods of rain, showing transfer from rainwater to groundwater of these compounds [77]. Studies have shown that oil leakage and spillage from petroleum storage facilities have the potential to impact soil and vulnerable shallow groundwater system [78].

The world health organization [79] has recommended limits for certain PAHs in drinking water. The uncontaminated groundwater appears to have lowest PAHs concentrations of all natural waters, i.e., 0.001–0.010 ng l<sup>-1</sup> [80]. In public drinking water supplies, BaP is regulated with the maximum contaminant level, or MCL of 0.2 µg l<sup>-1</sup> [81].

### **1.7 PAHs degradation**

Degradation of PAHs in the environment includes: biodegradation, photo oxidation, and chemical oxidation adsorption to soil particles, leaching and bioaccumulation.

#### **1.7.1 Biodegradation**

Biodegradation of PAHs was the most commonly studied degradation process described in the literature [82]. Microorganisms, for example bacteria and fungi, may transform the PAHs to other organic compounds or to inorganic end products like carbon dioxide and water. Various factors such as the presence of a microbial consortia capable of degrading the pollutant, the bioavailability of the contaminant to microbial attack and certain environmental factors (soil type, temperature, soil pH, oxygen level and nutrient content of soil) contributing to microbial growth effect the optimization of biodegradation process [83]. Bacterial species such as *Escherichia coli*, *Alcoligenes* sp., and *Thiobacter subterraneus* are concluded efficient isolates for degrading various PAHs compounds.

#### **1.7.2 Phytodegradation**

In phytodegradation process plants are used in-situ as well as their associated microorganisms to extract, sequester or detoxify pollutants from contaminated systems [84]. Research has indicated that various grasses and leguminous plants have

potential for phytodegradation of organics. Plants such as corn (*Zea mays*), alfalfa (*Medicago sativa*) and rape seed (*Brassica napus*) significantly boosted the adsorption of PAHs from contaminated soils [83].

### **1.7.3 Photolysis degradation**

Photolysis is defined as the destruction of a compound from reactions initiated by the absorption of light. These reactions occur when light absorbed by PAHs excites the electrons within the molecules that create an unstable structural arrangement. Subsequently, such unstable structural arrangement allows several physical and chemical processes to act on the compound [82].

### **1.7.4 Chemical degradation**

Chemical oxidation appears to be a minor PAH degradation mechanism under most environmental conditions. In the case of chemical oxidation, either naturally or as part of treatment technologies, the rates of PAH oxidation depend on several properties of the system. These properties includes, the molecular weight and structure of the compound, its physical state, temperature and the strength of the oxidizing agent [82].

## **1.8 PAHs and soil organic carbon**

Soil organic matter (SOM) or total organic carbon (TOC), plays a key role in the environmental partitioning, storage and longevity of hydrophobic organic contaminants (HOCs) like PAHs [85, 86]. Organic carbon may interact with PAHs by various mechanisms, which include physical and chemical adsorption, solubilisation, partitioning hydrolysis, photosensitisation and others [87]. Consequently, besides its chemical characteristics, the different fractions such as dissolved organic matter (DOM), fulvic acid (FA), humic acid (HA), and humin can affect the mobility of PAHs in soils. Numerous studies have found that soil organic carbon is the most important soil component for PAHs sorption. Hence the bioavailability and environmental persistence of PAHs are mostly affected by organic carbon [88].

## **1.9 PAHs and black carbon**

Black carbon (BC) is produced from incomplete combustion of fossil fuels and biomass, and from weathering of graphitic carbon in rocks, as the carbonaceous residue (e.g., charcoal) or condensate (e.g., soot) [89]. According to Druffel [90] approximately 62–294Tg BC were generated per year, of which 80–90% were deposited directly in soils and the rest were released into the atmosphere. BC has a great sorption capacity for some HOCs (e.g., at least 10–100 times) comparative to amorphous organic matter (AOM) and thus attracted considerable interest from environmental chemists [91]. The strong sorption of PAHs to BC reduces bioaccumulation in organisms and consequently lowers the actual risk of contaminated matrices. The environmental behavior, distribution and bioavailability of PAHs were strongly affected by BC [92, 93]. Various studies observed significant correlations between PAHs and BC, suggested their similar sources of origin [85, 94].

## **1.10 PAHs and heavy metals**

The PAHs have often been found to coexist with the metals due to similar sources of origin and it is well established that the combination of PAHs with heavy metal oxides turn into potent carcinogens [95].

Atmospheric dry and wet deposition is considered as the major pathways of anthropogenic inputs of heavy metals into the topsoil [96]. Long range atmospheric transport appears to have a profound impact on the deposition of heavy metals on surface soil. Normal geological phenomena such as ore formation, weathering of rocks may result extreme levels of heavy metals in the biosphere. Other activities that could contribute to discharge of these metals into the environment include burning of fossil fuels, smelting, and discharges of industrial, agricultural, and domestic wastes as well as deliberate application of pesticides [97]. Petroleum prospecting and mining as well as oil spillage are also considered as the major sources of these metals [98]. Crude oil contains heavy metals such as Cd, Pb, Ni, and V, and drilling fluid may also contain heavy metals like Cr, Pb, and Zn [99, 100]. The primary sources of groundwater contamination with heavy metals includes atmospheric precipitation, landfill leachate, sewage, leachate from mine tailings, deep-well disposal of liquid

wastes, seepage from industrial waste lagoons or from industrial spills and leaks [101].

### 1.11 Hypotheses of the study

1. Soils around oilfields are contaminated with organic pollutants like PAHs, which varies spatially and seasonally.
2. The surface soil contamination is the basis of contamination of groundwater with PAHs. There is surface to groundwater transport.
3. There are strong local sources of PAHs around the oilfield of upper Assam and long range transport of PAHs cannot be ruled out.
4. Association of OC, BC and heavy metals can give clues to the sources of PAHs of oilfields of upper Assam.

### 1.12 Background and Objectives of the study

Studies on soil PAHs is going on throughout the world. In India also research on soil PAHs has been carried out in a large scale in the major cities and industrial areas. However, studies on PAHs concentration of soil and groundwater in oilfield area are sporadic. Nevertheless, no study has been initiated in the oilfield area of Northeastern region although; the contamination of oilfield soils of Assam had possibly begun more than 100 years ago when the Asia's first oil well was drilled in 1889. With this background the present study was designed to focus on the PAHs loading in soil and groundwater around two oilfields; Borholla and Nambar in North-east India with the following objectives:

1. To understand the spatial and seasonal distributions of PAHs and some heavy metals in surface soil and groundwater around oilfields of upper Assam.
2. To understand the nature of the sources of PAHs in the oilfield areas.
3. To evaluate the ecological risk of PAHs and heavy metals.

4. To establish association of PAHs signatures in surface soil to PAHs signature in groundwater to understand the mode of transport of PAHs from surface soil to the groundwater.

### **1.13 Scope of the study**

The study will mainly focused on the levels of PAHs and heavy metals in surface soil and groundwater around two oilfields of upper Assam; Borholla and Nambar. Assessment of soil and groundwater had been done for two years long cycle around Borholla oilfield and for one year around Nambar oilfield and explored the seasonal trends and possible sources of PAHs and heavy metals. Sample analysis mainly focused on PAHs, heavy metals, OC and BC. Back trajectory analysis was carried out along with the temperature inversion plots to find out the influence of atmospheric condition on the seasonal variation of PAHs concentrations. Various PAHs diagnostic ratios were used for qualitative assessment of the PAHs sources. Statistical model-PCA-MLR (principal component analysis- multiple linear regressions) was used for source identification and to calculate the respective contribution of each source. Association of PAHs with OC, BC, heavy metals and some major ions were also built to identify their common source of origin.

Colloid facilitated transport was identified as the main route of PAHs transport into groundwater. Associations of various organic and inorganic constituents with PAHs in groundwater were also find out along with the association between PAHs signatures in surface soil to PAHs signature in groundwater in different seasons to understand the transport of PAHs from surface soil to groundwater via mobile colloids. We had also compared the present study with studies from other parts of India and abroad.

### **1.14 Innovation and contribution to knowledge**

This study being the first comprehensive one to evaluate the PAHs and heavy metal pollution in soils and groundwater around oilfields of this region and this study could provide the necessary ingredients for larger systematic studies on PAHs in the region.



**References**

1. Sakawa, Y. and Hashimoto, Y. Control of environmental pollution and economic growth: Modelling and numerical solution. *Applied Mathematics and Optimization*, 4 (1): 385-400, 1977.
2. Naspinski, C., Lingenfelter, R., Cizmas, L., Naufal, Z., He, L.Y., Islamzadeh, A., Li, Z., Li, Z., McDonald, T. and Donnelly, K.C. A comparison of concentrations of polycyclic aromatic compounds detected in dust samples from various regions of the world. *Environment international*, 34 (7): 988-993, 2008.
3. Jiang, Y., Zhao, C.C. and Zhao, D.F. Characteristic of oily sludge and several treatment methods. *Environ Protect Oily Gas Fields*, 15 (4): 38-41, 2005.
4. Kuang, S. and Xu, Z. Pollution characteristics of polycyclic aromatic hydrocarbons (PAHs) in oily sludge from the Zhongyuan Oilfield and its peripheral soils. *Chinese Journal of Geochemistry*, 28 (2): 176-183, 2009.
5. Du, X., Liu, J., Xin, J., Li, Y., Li, X. and Lang, Y. Polycyclic Aromatic Hydrocarbons (PAHs) in Soils Sampled from an Oilfield: Analytical Method by GC-MS, Distribution, Profile, Sources and Impacts. *Bioinformatics and Biomedical Engineering (iCBBE)*, 4th International Conference on IEEE, 1-4, 2010.
6. Nganje, T.N., Edet, A.E., Ibok, U.J., Ukpabio, E.J., Ibe, K.A. and Neji, P. Polycyclic aromatic hydrocarbons in surface water and soil in the vicinity of fuel-oil spillage from a tank farm distribution facility, EsukUtan, Calabar Municipality, Nigeria, *Environmental Earth Sciences*, 67 (1): 81-90, 2012.
7. Nganje, T.N., Edet, A.E. and Ekwere, S.J. Distribution of polycyclic aromatic hydrocarbon in surface soils from petroleum handling facilities in Calabar Metropolis, Southeastern Nigeria, *Environmental monitoring and assessment*, 130: 27-34, 2007.
8. Fetzer, J.C. *The Chemistry and Analysis of the Large Polycyclic Aromatic Hydrocarbons*, Wiley, New York, 2000.

9. Li, B., Zeng, F., Ma, W., Dong, Q., Fan, H. and Deng, C. Vertical Pollution Characteristics of PAHs around an Oil Sludge Storage Site of Jiangnan Oil Field of China, *Procedia Environmental Sciences*, 11: 1285-1290, 2011.
10. Gondal, M.A., Hussain, T., Yamani, Z.H. and Baig, M.A. Detection of heavy metals in Arabian crude oil residue using laser induced breakdown spectroscopy, *Talanta*, 69 (5): 1072-1078, 2006.
11. Tiwari, K.K., Singh, N.K., Patel, M.P., Tiwari, M.R. and Rai, U.N. Metal contamination of soil and translocation in vegetables growing under industrial wastewater irrigated agricultural field of Vadodara, Gujarat, India, *Ecotoxicology and environmental safety*, 74 (6): 1670-1677, 2011.
12. IARC. Approaches to classifying chemical carcinogens according to the mechanism of action, IARC intern. *tech. rep.* No. 83/001, 1983.
13. Shin, K.H., Kim, K.W. and Ahn, Y. Use of biosurfactant to remediate phenanthrene-contaminated soil by the combined solubilization- biodegradation process, *Journal of hazardous materials*, 137: 1831-1837, 2006.
14. Heitkamp, M.A. and Cerniglia, C.E. Polycyclic aromatic hydrocarbon degradation by a mycobacterium sp. in microcosms containing sediment and water from a pristine ecosystem, *Applied and Environmental Microbiology*, 55: 1968-1973, 1989.
15. Balati, A., Shahbazi, A., Amini, M.M. and Hashemi, S.H. Adsorption of polycyclic aromatic hydrocarbons from wastewater by using silica-based organic-inorganic nanohybrid material, *Journal of Water Reuse and Desalination*, 5: 50, 2015.
16. USEPA, Sampling and analysis procedures for screening of industrial effluents for priority pollutants. U. S. Environmental Protection Agency, Environment Monitoring and Support Laboratory, Cincinnati, 1977.
17. Hussain, K. and Hoque, R.R. Seasonal attributes of urban soil PAHs of the Brahmaputra Valley, *Chemosphere*, 119: 794-802, 2015.
18. USEPA, Polycyclic Organic Matter, US Environmental Protection Agency, 2002.

19. Singh, K.P., Malik, A., Kumar, R., Saxena, P. and Sinha, S. Receptor modeling for source apportionment of polycyclic aromatic hydrocarbons in urban atmosphere, *Environmental monitoring and assessment*, 136 (1-3): 183-196, 2008.
20. Maliszewska-Kordybach, B. Sources, concentrations, fate and effects of polycyclic aromatic hydrocarbons (PAHs) in the environment. Part A: PAHs in air, *Polish Journal of Environmental Studies*, 8: 131-136, 1999.
21. Kannan, K. and Perrotta, E. Polycyclic aromatic hydrocarbons (PAHs) in livers of California sea otters, *Chemosphere* 71(4): 649-655, 2008.
22. Cheruiyot, N.K., Lee, W.J., Mwangi, J.K., Wang, L.C., Lin, N.H., Lin, Y.C., Cao, J., Zhang, R. and Chang-Chien, G.P. An Overview: Polycyclic Aromatic Hydrocarbon Emissions from the Stationary and Mobile Sources and in the Ambient Air, *Aerosol and Air Quality Research*, 15: 2730-2762, 2015.
23. Skupinska, K.A., Misiewicz, I. and Kasprzycka-Guttman, T., Polycyclic aromatic hydrocarbons: physicochemical properties, environmental appearance and impact on living organisms, *Acta Poloniae Pharmaceutica*, 61 (3): 233-40, 2004.
24. Wania, F. and Mackay, D. Tracking the distribution of persistent organic pollutants, *Environmental Science & Technology* 30: 390A-396A, 1996.
25. Zakaria, M. P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E. and Kumata, H.D. Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs, *Environmental Science & Technology*, 36:1907-1918, 2002
26. Stogiannidis, E. and Laane, R., *Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: an overview of possibilities*, In Reviews of environmental contamination and toxicology, Springer International Publishing, 49-133, 2015.
27. Jones, D.M., Rowland, S.J., Douglas, A.G. and Howells, S. An examination of the Fate of Nigerian crude oil in surface sediments of the Humber estuary by gas chromatography and gas chromatography–mass spectrometry, *International Journal of Environmental and Analytical Chemistry*, 24: 227-247, 1986.

28. Lee, B.K. and Vu, V.T. *Sources, Distribution and Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs) in Particulate Matter, Air Pollution*, Villanyi Vanda, ed., ISBN: 978-953-307-143-5, 2010. Available from <http://www.intechopen.com/books/air-pollution/sources-distribution-and-toxicity-of-polyaromatic-hydrocarbons-pahs-in-particulate-matter>.
29. Zhang, Y. and Tao, S. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004, *Atmospheric Environment*, 43 (4): 812-819, 2009.
30. Guo, Y. Sources, distribution, and toxicity of polycyclic aromatic hydrocarbons, *Journal of environmental health*, 73 (9), 22, 2011.
31. Gupta, P., Banerjee, D.K., Bhargava, S.K., Kaul, R. and Ravi Shankar, V. Prevalence of impaired lung function in rubber manufacturing factory workers exposed to benzo(a)pyrene and respirable particulate matter, *Indoor and Built Environment*, 2: 26-31, 1993.
32. Eisler, R. Polycyclic Aromatic Hydrocarbon Hazards to Fish, Wildlife, and Invertebrates: a synoptic review, *US fish and wildlife service biological report* 85 (1.11): 81, 1987.
33. Alomirah, H., Al-Zenki, S., Al-Hooti, S., Zaghloul, S., Sawaya, W., Ahmed, N. and Kannan, K. Concentrations and dietary exposure to polycyclic aromatic hydrocarbons (PAHs) from grilled and smoked foods. *Food control*, 22(12): 2028-2035, 2011.
34. USEPA, Polycyclic Aromatic Hydrocarbons (Pahs) Fact Sheet. National Center for Environmental Assessment, Office of Research and Development, Washington, DC, 2008.
35. Xu, J. and Sparks, D.L. Adsorption of Dissolved Organic Compounds by Black Carbon. In *Molecular Environmental Soil Science*, pages 359-385. Springer, 2013.
36. Hussain, K., Balachandran, S. and Hoque, R.R., Sources of polycyclic aromatic hydrocarbons in sediments of the Bharalu River, a tributary of the River Brahmaputra in Guwahati, India. *Ecotoxicology and environmental safety*, 122, 61-67, 2015.

37. Munoz, B. and Albores, A. DNA damage caused by polycyclic aromatic hydrocarbons: mechanisms and markers. In *Selected Topics in DNA Repair*. InTech., 2011.
38. US. Environmental Protection Agency. Polycyclic Aromatic Hydrocarbons, 2009, [http://www.epa.gov/sites/production/files/201403/documents/pahs\\_factsheet\\_cdc\\_2013](http://www.epa.gov/sites/production/files/201403/documents/pahs_factsheet_cdc_2013).
39. Kannan, K., Kober, J.L., Khim, J.S., Szymczyk, K., Falandysz, J. and Giesy, J.P. Polychlorinated biphenyls, polycyclic aromatic hydrocarbons and alkylphenols in sediments from the Odra River and its tributaries, Poland. *Toxicol. and Environ. Chem.*, 85(4-6): 51-60, 2003.
40. Kannan, K., Lee Kober, J., Kang, Y.S., Masunaga, S., Nakanishi, J., Ostaszewski, A. and Giesy, J.P. Polychlorinated naphthalenes, biphenyls, dibenzo-p-dioxins, and dibenzofurans as well as polycyclic aromatic hydrocarbons and alkylphenols in sediment from the Detroit and Rouge Rivers, Michigan, USA. *Environmental toxicology and chemistry*, 20(9): 1878-1889, 2001.
41. Sun, H., Zhang, Q. and Xu, Y. Polycyclic Aromatic Hydrocarbons Concentrations in Drinking Water in Villages along the Huai River in China and Their Association with High Cancer Incidence in Local Population. *BioMed research international*, 2015.
42. Bozlaker, A., Muezzinoglu, A. and Odabasi, M. Atmospheric concentrations, dry deposition and air–soil exchange of polycyclic aromatic hydrocarbons (PAHs) in an industrial region in Turkey. *Journal of Hazardous Materials*, 153 (3): 1093-1102, 2008.
43. Aamot, E., Steinnes, E. and Schmid, R. Polycyclic aromatic hydrocarbons in Norwegian forest soils; impact of long range atmospheric transport. *Environmental Pollution*, 92(3): 275-280, 1996.
44. Birgul, A., Tasdemir, Y. and Cindoruk, S.S. Atmospheric wet and dry deposition of polycyclic aromatic hydrocarbons (PAHs) determined using a modified sampler. *Atmospheric Research*, 101(1): 341-353, 2011.

45. Cousins, I.T., Beck, A.J. and Jones, K.C. A review of the process involved in the exchange of semi-volatile organic compounds (SVOC) across the air-soil interface. *Science of the Total Environment*, 228: 5-24, 1999.
46. Hiller, E., Jurkovic, L. and Bartal, M. Effect of temperature on the distribution of polycyclic aromatic hydrocarbons in soil and sediment. *Soil & Water Research*, 3 (4): 231-240, 2008.
47. U.S. EPA. Deposition of Air Pollutants to the Great Waters: Third Report to Congress. Office of Air Quality Planning and Standards, EPA-453/R-00-0005; June 2000.
48. Mai, B.X., Qi, S., Zeng, E.Y., Yang, Q., Zhang, G., Fu, J., Sheng, G., Peng, P. and Wang, Z. Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: assessment of input sources and transport pathways using compositional analysis. *Environmental Science and Technology*, 37: 4855-4863, 2003.
49. Lohmann, R. and Lammel, G. Adsorptive and absorptive contributions to the gas-particle partitioning of polycyclic aromatic hydrocarbons: State of knowledge and recommended parametrization for modeling. *Environmental science & technology*, 38 (14): 3793-3803, 2004.
50. Vione, D., Barra, S., de Gennaro, G., de Rienzo, M., Gilardoni, S., Perrone, M.G. and Pozzoli, L. Polycyclic aromatic hydrocarbons in the atmosphere: monitoring, sources, sinks and fate. II: Sinks and fate. *Annali di chimica*, 94 (4): 257-268, 2004.
51. Ma, J., Chen, Z., Wu, M., Feng, J., Horii, Y., Ohura, T. and Kannan, K. Airborne PM<sub>2.5</sub>/PM<sub>10</sub>-associated chlorinated polycyclic aromatic hydrocarbons and their parent compounds in a suburban area in Shanghai, China. *Environmental science & technology*, 47(14): 7615-7623, 2013.
52. Hong, W.J., Jia, H., Ma, W.L., Sinha, R.K., Moon, H.B., Nakata, H., Minh, N.H., Chi, K.H., Li, W.L., Kannan, K. and Sverko, E. Distribution, fate, inhalation exposure and lung cancer risk of atmospheric polycyclic aromatic hydrocarbons in some Asian countries. *Environmental science & technology*, 50(13):7163-7174, 2016.

53. Suess, M.J. The environmental load and cycle of polycyclic aromatic hydrocarbons. *Science of the Total Environment*, 6: 239-250, 1976.
54. Hoff, R.M., Strachan, W.M.J., Sweet, C.W., Chan, C.H., Shackleton, M. and Bidleman, T.F. Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994. *Atmospheric Environment*, 30:3505–3527, 1996.
55. Moon, H.B., Kannan, K., Lee, S.J. and Ok, G. Atmospheric deposition of polycyclic aromatic hydrocarbons in an urban and a suburban area of Korea from 2002 to 2004. *Archives of Environmental Contamination and Toxicology*, 51(4): 494-502, 2006.
56. 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. and Sun, R. Polycyclic aromatic hydrocarbons (PAHs) in agricultural soil and vegetables from Tianjin. *Science of the Total Environment*, 320 (1): 11-24, 2004.
57. Chung, N.J., Cho, J.Y., Park, S.W., Park, B.J., Hwang, S.A. and Park, T.I. Polycyclic aromatic hydrocarbons in soils and crops after irrigation of wastewater discharged from domestic sewage treatment plants. *Bulletin of environmental contamination and toxicology*, 81: 124-127, 2008.
58. Wild, S.R., & Jones, K.C. Polynuclear aromatic-hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. *Environmental Pollution*, 88: 91-108, 1995.
59. Lv, J., Shi, R., Cai, Y. and Liu, Y. Assessment of polycyclic aromatic hydrocarbons (PAHs) pollution in soil of suburban areas in Tianjin, China. *Bulletin of environmental contamination and toxicology*, 85 (1): 5-9, 2010.
60. Smith, D.J.T., Edelhauser, E.C. and Harrison, R.M. Polycyclic aromatic hydrocarbon concentrations in road dust and soil samples collected in the United Kingdom and Pakistan. *Environmental Technology*, 16: 45-53, 1995.
61. Agarwal, T. Concentration level, pattern and toxic potential of PAHs in traffic soil of Delhi, India. *Journal of Hazardous Materials*, 171: 894-900, 2009.

62. Vogt, N.B., Brakstad, F., Thrane, K., Nordenson, S., Krane, J., Aamot, E., Kolset, K., Esbensen, K. and Steinnes, E. Polycyclic aromatic hydrocarbons in soils and air: Statistical analysis and classification by the SIMCA method. *Environmental Science Technology*, 21: 35-44, 1987.
63. Chuang, J.C., et al. Callahan, P.J., Menton, R.G., Gordon, S.M., Lewis, R.G. and Wilson, N.K. Monitoring methods for polycyclic aromatic hydrocarbons and their distribution in house dust and track in soil. *Environmental Science Technology*, 29: 494-500, 1995.
64. Takada, H., Onda, T. and Ogura, N. Determination of polycyclic aromatic by capillary gas chromatography. *Environmental Science Technology*, 24: 1179-1186, 1990.
65. Essumang, D.K., Dodoo, D.K., Obiri, S. and Oduro, A.K. Analysis of Polycyclic aromatic hydrocarbons in street soil dust in Kumasi metropolis of Ghana. *Environmental Monitoring Assessment*, 121: 401-408, 2006.
66. Wang, D. and Meresz, O. Occurrence and potential uptake of polynuclear aromatic hydrocarbons of highway traffic origin by proximal grown food crops. In Cooke, M. and Dennis, A. J., editors, *Polynuclear aromatic hydrocarbons: physical and biological chemistry*, pages 885-896, NY: Batelle Press, Columbus, 1982.
67. Reilley, K.A., Banks, M.K. and Schwab, A.P. Dissipation of polycyclic aromatic hydrocarbons in the rhizosphere. *Journal of Environmental Quality*, 25: 212-219, 1996.
68. Menzie, C.A., Potocki, B.B. and Santodonato, J. Exposure to carcinogenic PAHs in the environment. *Environmental Science & Technology*, 26 (7): 1278-1284, 1992.
69. Kanaly, R.A. and Harayama, S. Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. *Journal of bacteriology*, 182 (8): 2059-2067, 2000.



70. Golomb, D., Ryan, D., Eby, N., Underhill, J. and Zemba, S. Atmospheric deposition of toxics onto Massachusetts Bay-I. Metals. *Atmospheric Environment*, 31(9): 1349-1359, 1997.
71. Sharma, R.S. and Al-Busaidi, T.S. Groundwater pollution due to a tailings Dam. *Engineering Geology*, 60: 235-244, 2001.
72. Kannan, K., Johnson-Restrepo, B., Yohn, S.S., Giesy, J.P. and Long, D.T. Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from Michigan inland lakes. *Environmental science & technology*, 39(13): 4700-4706, 2005.
73. Masih, A., Lal, J.K. and Patel, D.K. Contamination and Exposure Profiles of Persistent Organic Pollutants (PAHs and OCPs) in Groundwater at a Terai Belt of North India. *Water Quality, Exposure and Health*, 6 (4): 187-198, 2014.
74. Osborne, M.R. and Crosby, N.T. *Benzopyrenes*. Cambridge University Press, Cambridge, 1987.
75. Kalmykova, Y., Bjorklund, K., Strömvall, A.M. and Blom, L. Partitioning of polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachates and stormwater. *Water research*, 47 (3): 1317-1328, 2013.
76. Abolfazi, M. and Elahe, A.P. Groundwater Quality and the Sources of Pollution in Baghan Watershed, Iran. *Journal of World Academy of Science*, 43: 28, 2008.
77. Schrimppff, E. Organic micropollutants' balances in watersheds of Northeastern Bavaria. *Fresenius' ZeitschriftfüranalytischeChemie*, 319 (2): 147-151, 1984.
78. Riccardi, C., Di Filippo, P., Pomata, D., Incoronato, F., Di Basilio, M., Papini, M.P. and Spicaglia, S. Characterization and distribution of petroleum hydrocarbons and heavy metals in groundwater from three Italian tank farms. *Science of the total Environment*, 393 (1): 50-63, 2008.
79. WHO. 2-Phenylphenol and its sodium salt in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality. Geneva, World Health Organization (WHO/SDE/WSH/03.04/69), 2003.

80. Dickhut, R.M. and Gustafson, K.E. Atmospheric inputs of selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls to southern Chesapeake Bay. *Marine Pollution Bulletin*, 30 (6): 385-396, 1995.
81. U.S. Environmental Protection Agency. "Drinking Water Contaminants." 2003. Available at. <http://www.epa.gov/safewater/contaminants/index.html>.
82. Abdel-Shafy, H.I. and Mansour, M.S. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 25 (1): 107-123, 2016.
83. Ukiwe, L.N., Egereonu, U.U., Njoku, P.C., Nwoko, C.I. and Allinor, J.I. Polycyclic aromatic hydrocarbons degradation techniques: a review. *International Journal of Chemistry*, 5 (4): 43, 2013.
84. Epuri, V. and Sorensen, D. *Benzo(a) pyrene and Hexachlorobiphenyl Contaminated Soil: Phytoremediation Potential*, Washinton DC: American Chemical Society Press, 6th ed., 15, 1997.
85. Nam, J.J., Song, B.H., Eom, K.C., Lee, S.H. and Smith, A. Distribution of polycyclic aromatic hydrocarbons in agricultural soils in South Korea, *Chemosphere*, 50: 1281-1289, 2003.
86. Semple, K.T., Morriss, A.W.J. and Paton, G.I. Bioavailability of hydrophobic organic contaminants in soils: fundamental concepts and techniques for analysis. *European Journal of Soil Science*, 54: 809-818, 2003.
87. Senesi, N. Binding mechanisms of pesticides to soil humic substances. *Science of the Total Environment*, 123: 63-76, 1992.
88. Ahangar, A.G. Sorption of PAHs in the soil environment with emphasis on the role of soil organic matter: a review. *World Applied Sciences Journal*, 11 (7): 759-765, 2010.
89. Wang, Q., Liu, M., Yu, Y., Du, F. and Wang, X. Black carbon in soils from different land use areas of Shanghai, China: Level, sources and relationship with polycyclic aromatic hydrocarbons. *Applied Geochemistry*, 47: 36-43, 2014.

90. Druffel, E.R.M. Comments on the importance of black carbon in the global carbon cycle. *Marine Chemistry*, 92: 197-200, 2004.
91. Ray, S., Khillare, P.S., Kim, K.H. and Brown, R.J. Distribution, sources, and association of polycyclic aromatic hydrocarbons, black carbon, and total organic carbon in size-segregated soil samples along a background–urban–rural transect. *Environmental engineering science*, 29 (11): 1008-1019, 2012.
92. Gustafsson, O., Haghseta, F., Chan, C., MacFarlane, J. and Gschwend, P.M. Quantification of the dilute sedimentary soot phase: implications of PAH speciation and bioavailability. *Environmental Science and Technology*, 31: 203-209, 1997.
93. Koelmans, A.A., Jonker, M.T., Cornelissen, G., Bucheli, T.D., Van Noort, P.C. and Gustafsson, O. Black carbon: the reverse of its dark side. *Chemosphere*, 63: 365-377, 2006.
94. Agarwal, T. and Bucheli, T. D. Is black carbon a better predictor of polycyclic aromatic hydrocarbon distribution in soils than total organic carbon? *Environmental Pollution*, 159: 64-70, 2011.
95. Garcon, G., Garry, S., Gosset, P., Zerimech, F., Martin, A., Hannotiaux, M.H. and Shirali, P. Benzo(a)pyrene-coated onto Fe<sub>2</sub>O<sub>3</sub> particles-induced lung tissue injury: role of free radicals. *Cancer letters*, 167(1): 7-15, 2001.
96. Chen, T. B., Zheng, Y.M., Lei, M., Huang, Z.C., Wu, H.T., Chen, H., Fan, K.K., Yu, K., Wu, X. and Tian, Q.Z. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. *Chemosphere*, 60 (4): 542-551, 2005.
97. Deka, J., Sarma, K.P. and Hoque, R.R. Application of multivariate statistical approach to identify heavy metal sources in oilfield soil of Brahmaputra Valley. *International journal of bio-resource, environment and agricultural sciences*, 1(4): 199-215, 2015.
98. Osuji, L.C. and Onojake, C.M. Trace Heavy Metals Associated with Crude Oil: A Case Study of Ebocha-8 Oil-Spill-Polluted Site in Niger Delta, Nigeria. *Chemistry & biodiversity*, 1 (11): 1708-1715, 2004.

99. Fu, X., Cui, Z. and Zang, G. Migration, speciation and distribution of heavy metals in an oil-polluted soil affected by crude oil extraction processes, *Environmental Science: Processes & Impacts* 16 (7), 1737-1744, 2014.
100. Krzyzanowski, J. Environmental pathways of potential impacts to human health from oil and gas development in northeast British Columbia, Canada. *Environmental Reviews*, 20 (2): 122-134, 2012.
101. Hashim, R., Kamali, B., Tamin, N.M. and Zakaria, R. An integrated approach to coastal rehabilitation: mangrove restoration in Sungai Haji Dorani, Malaysia. *Estuarine, Coastal and Shelf Science*, 86 (1): 118-124, 2010.