



Chapter 2

REVIEW OF LITERATURE

Concerns over the adverse effects of Polycyclic Aromatic Hydrocarbons (PAHs) in human health and environment, results their extensive studies all throughout the World. Studies on PAHs deposition on surface soil has been reported by numerous researchers for last three to four decades. However study on PAHs contamination in groundwater is limited. Integrated data on PAHs, heavy metals and carbon concentrations in soils and groundwater yielded synergistic information that could be interpreted in terms of PAHs emission sources, transport and spatial distribution.

2.1 Worldwide scenario of PAHs

2.1.1 PAHs in surface soil

Among the earlier studies, Youngblood and Blumer [1] conducted a study on presence of PAHs in surface soil in 1975. They reported that these hydrocarbons are produced in natural fires, dispersed and transported through air and later on deposited onto various surfaces. In 1989 Jones et al. [2] determined the total concentration of 14 PAHs in surface soil of Wales, which ranged from 100 to 55,000 $\mu\text{g kg}^{-1}$. Samples were taken along a gradient of remote-rural-urban locations showed an increase in soil PAHs. Fluoranthene was the most abundant of all the measured PAHs. Soil organic matter content had showed a great influence over soil ΣPAHs concentrations. A higher ΣPAHs concentration was observed in soils naturally rich in organic matter, like peat bogs or deciduous and coniferous woodland soils.

Wilcke et al. [3] estimated the concentrations of 20 PAHs in hydromorphic urban surface soil of tropical metropolis, Bangkok. The ΣPAHs concentrations ranged between 12 and 380 $\mu\text{g kg}^{-1}$; far lower than in soils of temperate cities. The dominant PAH was Nap contributing 14% of the total PAHs concentration. They concluded that enhanced biodegradation, volatilization, photo-oxidation and leaching into the groundwater in the tropical climate may be the reason of lower PAHs concentration.

A study on vertical distribution of soil PAHs in different particle-size fractions showed that the fine silt fraction contained higher PAHs level than sand and coarse silt fraction [4]. This difference in concentration was due to the fact that PAHs in macroporous fractions were susceptible to volatilize or degrade compared with that in

microporous fractions. The study also reported that the vertical transport of PAHs in soils was controlled by the properties of PAHs (i.e. log K_{ow}, molecular weight), soil particle size and soil organic matter contents.

Spatial variation of PAHs in surface soils from five different locations in Klang Valley, Malaysia was investigated by Lau et al. [5]. The total concentrations of 14 priority PAHs was found in the range from 64 to 155 $\mu\text{g kg}^{-1}$. Results showed that regardless of the land use pattern, all the measured soil PAHs concentrations were significantly lower than that found in soil samples in temperate forest regions. The profile of PAHs in the soils was dominated by the 3-ring PAHs in most of the sampling sites. The PAHs source in soil of Klang Valley was found to be originated from pyrogenic sources, with a combination of petroleum and biomass combustion in vehicles, industries and non-point sources. Saba et al. [6] also found dominance of LMWPAHs with 3-4 ring structures in PAHs compositional profile of surface soil samples from an area adjacent to petrochemical plant in Rawalpindi Pakistan. The ratios of Phe/Ant reflected the pyrogenic origin of PAHs in the study. The relationship of PAHs with TOC has also been investigated and a positive correlation was observed between ΣPAHs and TOC.

Yuan et al. [7] measured the PAHs concentrations in 61 surface soil samples collected from the Yellow River Delta (YRD), China. The total PAHs flux ranged from 27 - 753 $\mu\text{g kg}^{-1}$, with a mean of $118 \pm 132 \mu\text{g kg}^{-1}$. The maximum concentration was noticed in the mid-southern part of the YRD (753 $\mu\text{g kg}^{-1}$), which was associated with the oil exploration. The diagnostic ratio studies indicated that the PAHs throughout the YRD were mostly of pyrogenic origin; while various sites in mid-southern part in the region were resultant from the petrogenic sources. Multivariate statistical analyses confirmed that the PAHs in surface soils of the YRD were mainly from the coal and biomass combustion, petroleum spills, and/or vehicular emissions. The PAHs toxicity analysis revealed that the PAHs in soils were at low potential of ecotoxicological contamination level for the YRD.

The PAHs concentration on surface soil was also measured in remote areas like Tibetan Plateau (TP) by Wang et al. in 2007 [8]. Concentrations of PAHs ranged from 5.54 to 389 $\mu\text{g kg}^{-1}$ with an average of 59.9 $\mu\text{g kg}^{-1}$, the values were relatively lower compared to other parts of the world, implying the TP is comparatively pristine.

Elevation was found to play a significant role in determining the spatial distribution of soil PAHs. The long range atmospheric transport (LRAT) by prevailing wind is considered as the main pathway that inputs pollutants to the plateau along with domestic activities like burning of yak dung and wood. The air- soil exchange indicated that the soils of the TP will act as a sink for HMWPAHs, but may turn into a possible “secondary source” for LMWPAHs.

Shi et al. [9] estimated the distribution of 16PAHs in industrial, traffic, rubbish, gas station, residential, and suburban areas of the surface soils of Baise, in southwest China between June and November 2013. The average concentrations of Σ PAHs varied significantly, depending on the sampling location and ranged from 16.8 to 6,400 $\mu\text{g kg}^{-1}$ (dry weight basis), with a mean value of 566 $\mu\text{g kg}^{-1}$. A decreased in PAHs concentrations was noticed along the industry-traffic-rubbish-gas station-residential-suburban transect. The sampling site profiles in the industrial, rubbish, and residential areas were ruled by four-ring PAHs, whereas five-ring PAHs were the major components in the traffic zones. Two ring PAHs dominated the gas station fields, whereas three-ring PAHs dominated the suburban sites. The PAHs profiles denoted that their distribution in surface soil was influenced by source proximity to the sampling sites, or transport and deposition effects. Similar study was conducted by Mizwar et al. [10] in surface soils of three different coal stockpile, agricultural and residential sites in South Kalimantan Province, Indonesia. Total PAHs concentration ranged from 4690 to 22700 $\mu\text{g kg}^{-1}$. Higher PAHs concentrations was observed at the surface soil samples of coal stockpile sites compared to those in agricultural and residential soil. A mixture of petrogenic and pyrogenic sources was found within the study area, as suggested by the isomeric ratios of PAHs. The results of PCA/MLR showed that three sources contributed to the PAHs in the study area, including biomass and coal combustion, raw coal and vehicular emission. The high value of BaPeq suggested that local residents were exposed to a high carcinogenic potential.

2.1.2 PAHs in Groundwater

Groundwater is considered as an important source of drinking water for human being. The assessment of chemical composition of groundwater is essential to examine its degree of suitability as a source of water for human and animal consumption, irrigation and for industrial and other purposes [11]. The quality of groundwater

mirrors inputs from the atmosphere, from soil and rock - water interactions along with pollutants from agriculture, land clearance, domestic and industrial effluents, mining, acid precipitation [12]. Contamination of groundwater with synthetic organic materials is triggering major environmental problems in many areas of the industrialized nations. At present much interest is focused in evaluating the nature and extent of groundwater contamination from toxic or hazardous organic pollutants [13, 14].

Martens et al. [15] determined the concentration and distribution of PAHs in groundwater of a rural region in Bavaria, Germany in 1990. Compounds like Nap and Phe were found to be predominant in groundwater. The study reported that the distributions of PAHs were the result of different transport mechanisms as, 2- and 3-ring PAHs are transported mainly in the dissolved or gaseous state whereas the 4- to 6 ring PAHs mainly through the particle or colloid-associated state.

The PAHs flux was evaluated in groundwater at a mid-Atlantic coal tar site between December 1995 and September 1996 [16]. Results showed that PAHs concentration at a coal tar site were raised by factors from 3 (Pyr) to 50 (IcdP) over purely dissolved concentrations. The low groundwater turbidities and small colloid particle sizes suggest that the PAHs observed in the bulk groundwater were mobile. Similarly, groundwater samples of the monitoring wells of gasoline stations were studied from Rio de Janeiro City, Brazil during 2003 and 2004 [17]. Total PAHs concentrations ranged between 0.05 and 84.9 ng ml⁻¹ in 2003 and 0.25 and 54.6 ng ml⁻¹ in 2004. Naphthalene was the predominating PAH and it was found in all samples with concentrations between 0.20 and 83.4 ng ml⁻¹ in 2003 and between 0.116 and 20.5 ng ml⁻¹ in 2004. The concentrations of BaP in all the samples were below its maximum concentration limits (MCL) in drinking water adopted by the Brazilian Regulation. The study concluded that PAHs present in some of the locations leading to a deterioration of groundwater quality.

Study on distribution and risk assessment of PAHs in drinking water resources have been carried out in Henan Province, China by Ma et al. [18] during May, August and November, 2001. Total concentration of 16 PAHs in the study area ranged from 15 to 844 ng ml⁻¹ with a mean value of 178±210 ng ml⁻¹. Higher concentrations of total PAHs were observed in August and November than in May. Evaluation of the

possible sources of PAH contamination by diagnostic ratio indicated that the coal combustion sources were the main contributors to PAHs in most drinking water resources. Some petrogenic sources of PAHs were also found. Study concluded that PAHs for drinking water resources in Henan province showed some carcinogenic potential. Another study on PAHs concentrations in groundwater samples, collected from the 12th coal mine around gangue piles in Henan Province, China, were estimated by Wang et al. [19]. The concentrations of PAHs in the leachate from different weathered gangues were compared with PAHs concentration in groundwater to investigate the pollution effects of PAHs from leachate on groundwater. The total concentrations of 16 USEPA PAHs ranged from 0.147 to 1.22 ng ml⁻¹. The PAHs profile was dominated by the 2- and 4- ring PAHs whereas; PAHs such as Chr, BaA, BbF, BkF, IcdP and DaA were fairly high. This may be due to the transport of LMWPAHs leached by rains from the coal mines after landfilling and dumping. Ansa-Asare [20] also found Nap as abundant species in the groundwater at the site of a fuel service station.

To understand the deleterious effects caused by wastewater, broadly used for agricultural irrigation in china twenty-three groundwater samples were collected and analysed for PAHs concentration [21]. Mean concentrations of 16 PAHs ranged from 3.67-25.7 ng ml⁻¹ in the groundwater samples. Maximum PAHs concentration was observed in case of BaA and BkF, as they were easily adsorbed to the colloidal phase particles. The study concluded that PAHs concentration in groundwater was due to the contaminated soils irrigated with wastewater discharged from petrochemical factory.

Similar study was carried out by Saba et al. [6] on groundwater samples collected from an area adjacent to petrochemical plant in Pakistan. Concentrations of six PAHs, Nap, Ace, Phe, Ant, Fla, and Chr were ranged from 0.201-1.63 ng ml⁻¹ (average: 0.763 ± 0.377 ng ml⁻¹). The PAHs profile was dominated by 3- to 4- ring PAHs. Positive correlation was observed between ΣPAHs and TOC which indicates that partitioned in organic matter may be the possible source of PAHs in water. An assessment using widely cited guidelines indicated that water samples do not pose biological impact.

Kalmykova et al. [22] studied partitioning of PAHs in landfill leachates and storm water in the Gothenburg region, Sweden in between 1936–1976. A statistically significant difference was observed between total, dissolved and colloid-bound fraction for three of the PAHs; Nap, Phe and Fla. The K_{OW} value negatively correlated with occurrence and concentrations of pollutants in dissolved and colloid-bound phases. The results confirm that the compounds partitioning and binding process to dissolved organic carbon (DOC) is well described by the K_{OW} values of specific organic pollutants.

2.2 Indian Scenario of PAHs

Like many other countries around the world, in India also researchers take initiative in the study of PAHs from the earliest years. Now-a-days, scientists from various parts of the country started the assessment of PAHs in different environmental matrices like air, water and soil.

2.2.1 PAHs in surface soil

Masih and Taneja [23] conducted a study in surface soil at four locations including industrial, residential, roadside and agricultural areas in Agra to assess the PAHs contamination levels for a span of one year. The total PAHs concentrations in industrial ($13.7 \mu\text{g g}^{-1}$) and roadside ($12.9 \mu\text{g g}^{-1}$) soil were less than the concentrations found in Austria ($79.0 \mu\text{g g}^{-1}$) [24], Germany ($16.0 \mu\text{g g}^{-1}$) [25] and the USA ($58.6 \mu\text{g g}^{-1}$) [26], respectively, while residential ($9.37 \mu\text{g g}^{-1}$) and agricultural ($6.73 \mu\text{g g}^{-1}$) sites PAHs concentrations showed higher than in the UK ($4.20 \mu\text{g g}^{-1}$) [27] and Germany ($1.90 \mu\text{g g}^{-1}$) [24] respectively. Maximum PAHs concentrations were found in winter season. In all the sites Chr and BbF were the dominant compounds.

The level of PAHs contamination due to jet turbine exhaust in the peripheral soil of the International Airport in Delhi, India was determined by Ray et al. [28]. The sampling site near landing point revealed maximum concentration of PAHs, while minimum concentration was observed at the site near take-off point. The Σ PAHs concentration detected was ~ 2.58 times higher than that of the background (BG) site.

Atmospheric deposition was considered as the most common source of soil PAHs contamination. Predominance of Pyr was noticed in the airport soil. The PAHs composition profile was dominated by 4- ring PAHs (41%).

Concentrations of Σ PAHs on traffic soil of Delhi determined by Agrawal [29] during winter season in the year 2006 were ranged from 1100 to 9700 $\mu\text{g kg}^{-1}$ with an average value of $4700 \pm 3000 \mu\text{g kg}^{-1}$ and found many fold higher than the rural site ($886 \pm 303 \mu\text{g kg}^{-1}$). Observed concentrations were similar to the PAHs content in the roadside soil of Brisbane, Australia, 3300 $\mu\text{g kg}^{-1}$ (Σ_{14} PAHs) [30] and Shanghai, China, 6280 $\mu\text{g kg}^{-1}$ (Σ_{16} PAHs) [31]. The PAHs profile was dominated by 5- and 6- ring PAHs (contributing >50% to the total PAHs) at the traffic sites whereas, rural soil revealed a predominance of 2- and 3-ring PAHs.

A study of PAHs pollution in roadside soil was conducted in Jalandhar city, Punjab during autumn and winter seasons in the year 2009 to ascertain the contamination levels and their distribution behavior in soil [32]. The average Σ PAHs concentration was found to be 4.04 and 16.4 $\mu\text{g g}^{-1}$ respectively. The highest concentration was recorded for DaA and BaP at all the sampling points ranging between 0.008 to 28.4 $\mu\text{g g}^{-1}$ during winter and 0.01 to 253 $\mu\text{g g}^{-1}$ during autumn. Average concentration of non-CPAHs and CPAHs during winter and autumn was found to be 2.1 and 6.4 and 4.74 and 35.1 $\mu\text{g g}^{-1}$ respectively. Total CPAHs concentration was found higher (80 %) compared to non-CPAHs (20 %) at most of the stations.

Sing et al. [33] evaluated the concentration of 16 PAHs in soil samples collected from four different sampling sites including industrial, roadside, residential and agricultural areas of Delhi. The PAHs concentrations at industrial and roadside soils indicated 3–7 times greater value in comparison to residential and agricultural soils. Industrial and roadside sites were dominated by 4- and 5-ring PAHs (contributing >50% to the total PAHs) with higher concentration of Fla, Chr, BbF, BkF, BaP, BgP, and Pyr while, 2- and 3-ring PAHs (Fla, Ace, Nap, Chr, and Ant) showed a predominance in residential and agricultural sites. Isomeric pair ratios suggested biomass combustion and fossil fuel emissions as the main sources of PAHs in the study.

Seasonal variation of PAHs concentration in urban soil of the Brahmaputra Valley was investigated by Hussain et al. [34] in 3 consecutive seasons, viz. monsoon (May), post-monsoon (November) and pre-monsoon (February), during 2011–12. Mean

concentrations of Σ PAHs were found to be highest during post-monsoon seasons followed by pre-monsoon and monsoon season. Total PAHs concentration of the study area ranged between 800 and 51300 ng g⁻¹ and comparable with studies reported from South Korea [35], Delhi [28, 29], Shanghai [36], Beijing [37] and Egypt [38]. Dominance of 2- and 4-ring PAHs was observed in the PAHs profile.

Suman et al. [39] examined the impact of vehicular traffic on the contamination status of urban traffic soils in Dhanbad City with respect to PAHs. Total PAHs concentration of 13 priority PAHs ranged from 1.02 $\mu\text{g g}^{-1}$ to 10.9 $\mu\text{g g}^{-1}$ with an average value of 3.49 $\mu\text{g g}^{-1}$ at traffic sites and 0.640 $\mu\text{g g}^{-1}$ at rural sites. The PAHs profile was dominated by 4- and 5-ring PAHs (contributing >50% to the total PAHs) at traffic sites, rural soil showed a predominance of LMWPAHs (3-ring) (contributing >30% to the total PAHs). Comparing to the control or rural soil the carcinogenic potency of PAHs load in traffic soil was almost 6.15 times higher. The results indicated that vehicular emission was the major source for PAHs contamination with moderate effect of coal combustion and biomass combustion.

2.2.2 PAHs in groundwater

A very limited study has been conducted on PAHs contamination of groundwater in India. Masih et al. [40] measured the concentration of 13 PAHs in groundwater at 12 locations of Agra in 2008. The concentration of Σ PAHs ranged from 13.2 to 64.3 ng lit⁻¹ with a mean of 31.9 ng l⁻¹. The carcinogenic potency was found to be 2.7 ng l⁻¹. Another study was conducted on groundwater PAHs concentrations at commercial site of Gorakhpur during winter season [41]. The total PAHs concentration ranged from 9.89 to 50.6 ng l⁻¹ with a mean and median value of 23.2 ng l⁻¹ and 8.02 ng l⁻¹ respectively. The PAHs profile was dominated by 3-, 4- and 5-ring PAHs having 41, 19 and 19% of the total PAHs respectively. Determination of toxic equivalent factor (TEFs) revealed that IcdP contributed the highest carcinogenic exposure equivalent (3.15 ng l⁻¹). The levels of PAHs in the groundwater can help in environmental risk assessment of this area.

2.3 PAHs in oilfield

2.3.1 PAHs in oilfield surface soil

Recently, studies of PAHs concentrations, distribution and risk assessment in soils have been conducted at different regional scales across the world. However, there has been less research on the concentration, distribution, and possible sources of PAHs in oilfield soils, as compared to urban, industrial and agricultural soils.

Accumulation and risk assessment of PAHs in oily sludge from Zhongyuan oilfield and its peripheral soil, China were investigated [42]. Compounds like Nap, Any, Ane, Flu and Phe were observed as the major pollutants in oily sludge. The PAHs concentration in soil samples around the oily sludge dumping sites varied from 435-2400 ng g⁻¹. A visible difference in the concentration levels of PAHs was observed in oilfield top soils from five different sampling sites of China in June 2009[43]. The concentrations of ΣPAHs in the soils ranged between 1340 and 82400 ng g⁻¹. The pattern of PAHs profile of soil samples followed the order: 5-ring> 4-ring>3-ring>2-ring. The soil samples collected near to oil platform were contaminated with high PAHs concentration and should be considered for remediation; however, levels of PAHs in the other sites were lower and could be used for various land use type.

Concentration of ΣPAHs in soil samples collected from different depth of Jiangan oilfield of China were as follows of 1300ng g⁻¹ (0-10 cm), 1600 ng g⁻¹ (10-20 cm), 1700 ng g⁻¹(20-30 cm), 1900 ng g⁻¹ (30-40 cm), 1130 ng g⁻¹ (40-50 cm), 739 ng g⁻¹ (50-60 cm), 387 ng g⁻¹(60-70 cm), 214 ng g⁻¹(70-80 cm), 149 ng g⁻¹ (80 -90 cm), 98 ng g⁻¹(90-100 cm) [44]. The results indicated that the study area was severely polluted by PAHs like Nap, Any, Flu, Phe, Chr, BbF, BkF, BaP, IcdP, DaA, BgP, while the amount of Ane, Fla, Pyr and BaA was comparatively low. The greatest value of PAHs appeared in the depth of 30-40 cm. Study confirmed that PAHs showed a strong capability to migrate downward. The ability of different PAHs components to transport downward follow the order: 2 ring >3 ring>4 ring>5 ring>6 ring PAHs.

Jiao et al. [45] reported ΣPAHs concentrations from Dagang oilfield, China in April 2013 which varied between 104 and 5900 μg kg⁻¹, with an average of 920μg kg⁻¹. The maximum PAHs concentrations were recorded at urban and residential zones followed by oil well areas and arable desert soil. About 22% of sampling sites were

identified as heavily contaminated, 22% as moderately contaminated, 37% as lightly contaminated and 19% as not contaminated. Two- and three-ring PAHs were regarded as the main components of pollution, with a corresponding mean ratio of 38.4 and 27.8% to total PAHs concentrations respectively. The total concentrations of CPAHs varied from 13.3 - 4400 $\mu\text{g kg}^{-1}$ for all samples, with an average of 594 $\mu\text{g kg}^{-1}$. The results indicated that the oilfield soil is exposed to a certain level of ecological risk. Similar study was carried out in four different oilfields across China (Daqing, DQ; Shengli, SL; Xinjiang, XJ; and Huabei, HB) reported that the most dominant components of all PAHs were Phe, Chr, and Pyr [46]. The seven possible CPAHs accounted for 8–25.7 % of the total PAHs. The PAH isomeric ratios indicated that PAHs in oil fields mainly originated from petroleum. The toxic assessment explained that people living and working in oilfields would suffer low carcinogenic risk.

Various studies indicated that oil spills around petroleum exploration and refinery areas in Nigeria were the major sources of PAHs pollution. Abbas et al. [47] investigated the distribution and sources of PAHs in soil at Niger Delta (Nigeria) in 21 soil samples (0- 10cm upper layer) collected in May, 2003. The soil samples were predominated by 2- and 3- ring aromatic hydrocarbons. Soil pollution by PAHs in two Niger Delta communities, Eleme (highly industrialized) and Ahoada East (less industrialized), Nigeria was assessed by Ana et al. [48]. The highest total PAHs concentration ($2.30 \times 10^6 \text{ ng kg}^{-1}$) was recorded in the samples adjacent to the petroleum refinery at Alesa (Eleme), even though the value was slightly lower than the EPA guideline value of $2.5 \times 10^6 \text{ ng kg}^{-1}$. The study showed that the communities at Eleme may be more susceptible to the threats associated with increased PAHs exposure compared to Ahoada East. The highest level of BaP was recorded at the heavily industrialized communities of Alesa, Ebubu and Onne at Eleme area. Nganje et al. [49] reported the concentration of Σ PAHs ranged from 4.28 to 29.8 mg kg^{-1} in the contaminated soils from two spilled sites of Calabar, Nigeria for the samples collected at depths of 15 to 100cm between the months of August and November 2000. They reported that PAHs concentration was decreased with depth. The obtained Σ PAHs concentrations were higher in comparison to the values attained from rural and semi urban soils, however lower than the values acquired from soils of some petroleum handling facilities of the study area. The soil of the study area was dominated by LMWPAHs.

Table 2.1 Soil PAHs concentrations (ng g⁻¹) reported from elsewhere.

Location	Number of PAHs	ΣPAHs conc.(ng g ⁻¹)	References
¹ Shanghai, China	16 PAHs	3280–38900	[36]
² Indira Gandhi International Airport, New Delhi	12 PAHs	2390–7530	[28]
⁴ Shanghai, China	22 PAHs	422-19700	[31]
	16 PAHs	347-17900	
³ Oilfield, China	16 PAHs	1340 – 82400	[43]
³ Jiangnan oilfield China	16 PAHs	98-1900	[44]
⁴ Switzerland	16 PAHs	32–8470	[29]
³ Zhongyuan oilfield, China	16 PAHs	434-2410	[42]
⁴ Klang Valley, Malaysia	14 PAHs	64 – 155	[5]
⁴ Egypt	16 PAHs	53.4–5560	[38]
¹ Guwahati, India	16 PAHs	799–51300	[34]
⁴ Baise, China	16 PAHs	16.8 - 6440	[9]
³ Dagang oilfield, China	16 PAHs	104- 5870	[45]
¹ Dhanbad City, India	13 PAHs	1020-10900	[39]
⁴ Indonesia	16 PAHs	4690 – 22700	[10]

¹Urban top soil; ²Peripheral soil of airport; ³Oilfield topsoil; ⁴Surface soil; ⁵Surrounding areas of oilfield.

2.3.2 PAHs in oilfield groundwater

Sixteen USEPA priority PAHs were analyzed for the groundwater samples in Nigeria [50]. The concentrations ranged from 1.92 - 40.5 µg l⁻¹, which was above the WHO recommended maximum limit for safe drinking water. Due to low water solubility HMWPAHs such as BgP, DaA and IcdP were mostly absent. High PAHs concentrations in the studied samples were found to cause health hazard to the population. Ogbuagu et al. [51] found concentration of six PAHs namely BbF, Fla, BkF, Pyr, BaA and Chr varied from 0.00037-0.512 (mean 0.081±0.03) mg l⁻¹, 0.0006-0.328 (mean 0.047±0.02) mg l⁻¹, 0.0002-0.084 (mean 0.023±0.01) mg l⁻¹, 0.0002 - 0.247 (mean 0.051±0.02) mg l⁻¹, 0.0002-0.219 (mean 0.051±0.02) mg l⁻¹, and 0.0001 - 0.165 (0.048±0.01)mg l⁻¹ respectively in a study carried out in Okrika mainland, Nigeria. Concentration of 7 PAHs evaluated by Gawad et al. [52] in Marmul area, Sultanate of Oman ranged between not detected to 0.806ppm. The highest concentration was showed by Nap (0.616ppm) and the lowest concentration was by Flu (0.004ppm).

Table 2.2 Concentration ranges of PAHs (ng ml⁻¹) reported from different groundwater sources worldwide.

Site	Period	Total studied PAHs	ΣPAHs conc. (ng ml ⁻¹)	References
¹ Nigeria Delta	-	16PAHs	1.92-40.45	[50]
² Accra, Ghana	-	18 PAHs	20.9 - 51.9	[20]
¹ Oilfield of Marmul area, Oman	2008	7PAHs	BDL -806	[52]
¹ Okrika Mainland, Nigeria	2010	6PAHs, Fluoranthene Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(k)fluoranthene	0.60 - 329 0.15 - 248 0.20 - 220 0.13 - 166 0.37 - 513 0.17 - 84.8	[51]
³ GW, Terai belt, North India	2010-2011	16 PAHs	0.010-0.044	[23]
⁴ Henan Province, China	-		0.147 – 1.22	[19]

2.4 Atmospheric signature of soil PAHs

Researchers also tried to estimate the atmospheric signature of soil PAHs from earlier. Jones et al. [53] reported from a study conducted at Rothamsted experimental station southeast England at various times since the mid-1800s that the total PAHs flux of the soil has increased approximately 4-fold since the 1880 to 1890s, with noticeable increase in some compounds like BbF, BkF, BaP, Pyr, BaA and IcdP. They found that the average increase in PAHs rates in the Rothamsted plots over the centuries were similar to contemporary atmospheric deposition rates to semirural locations.

Aamot et al. [54] concluded that PAHs concentration of soil samples from southern Norway were about ten-fold higher compared to central Norway with respect to 4- and 5- ring PAHs. Long-range atmospheric transport was considered as the major source of soil PAHs. This assumption was confirmed with the analyses of peat cores from ombrotrophic bogs, which provide a potentially useful method for temporal studies of atmospheric PAHs deposition. Higher concentration of Nap was observed in comparison to many other studies.

Spatial and temporal variation in the atmospheric deposition of PAHs into soil was examined by Wong et al. [55] in experimental soils and forest soils at several sites along an urban-rural transect of Toronto. Concentration of PAHs was decreased with

distance from the urban center by a factor of 2 for the experimental and 60 for forest soils respectively. The study used a dynamic model to assess the long-term uptake of PAHs in forest soils. The model indicated that LMWPAHs may attain equilibrium and become involved in soil-air exchange whereas HMWPAHs are stored for much longer time periods.

A study by Nam et al. [56] in 1998 reported the concentration of 16 PAHs ranged between 42 and 11200 μgkg^{-1} and 8.6 and 1050 μgkg^{-1} in the UK and Norwegian soil, respectively. The PAHs profile indicated that 90% of ΣPAHs in the UK soil and 50% in the Norwegian soil comprised of 4- and more rings. It indicated that the atmospheric transport and deposition was the main factor causing the fractionation occurred in PAHs profile. Due to low K_{ow} values the lighter PAHs were more readily reached the remote sites whereas, the heavier PAHs with higher K_{ow} values persisted in close to their sources.

Wang et al. [57] studied the air–soil gas exchange of PAHs in remote, rural village and urban areas of Beijing–Tianjin region, North China between 2007 and 2008 covering four seasons. The annual median air–soil gas exchange flux of PAHs from soil to air was recorded as 42.2 $\text{ngm}^{-2}\text{day}^{-1}$. Moreover, the air–soil gas exchange fluxes of PAHs at the urban sites were greater than those at the remote and rural sites. Due to high temperatures and increased rainfall in summer, more gaseous PAHs volatilized from soil to air. On the other hand, in winter, more gaseous PAHs deposited from air to soil due to high PAHs emissions and low temperatures. There is no significant influence of soil TOC concentration on the air–soil gas exchange of PAHs. Similar study was carried out in Izmir, Turkey between May 2003 and May 2004 indicated that Flu, Phe and Ant were deposited to soil in winter while they were volatilized in summer where, other compounds like Fla, BgP were deposited to soil in both periods [58]. Calculated gas-phase air–soil exchange fluxes showed that annual average fluxes of PAHs representing soil to air (i.e., gas volatilization) and air to soil transfer (i.e., gas absorption, dry deposition, and wet deposition) processes were comparable for 14PAHs however their input was dominated by gas absorption. For LMWPAHs, gas absorption was dominated and for HMWPAHs dry deposition was dominated process. Xiao et al. [59] also concluded that the long range transport of PAHs via atmosphere from urban area impact the PAHs distribution in the forest soils

of rural areas in the Pearl River Delta of Southern China in a study conducted from July to August 2013.

2.5 PAHs toxicity assessment

The PAHs are potentially toxic, carcinogenic and mutagenic to living organisms including plants and animals. The LMWPAHs are acutely toxic but non-carcinogenic, whereas the HMWPAHs are strongly carcinogenic and mutagenic to living organisms [60]. Among all the 16 priority PAHs, BaP has the highest carcinogenic potency and long-term persistency in the environment and used as an indicator of human exposure to PAHs [61]. According to the WHO [62], the permissible limit of BaP in ambient air is 1 ng/m³. Extensive reviews of potential exposures and health effects of PAHs and PAHs mixtures were carried out by the United States Agency for Toxic Substances and Disease Registry (ATSDR) [63], the International Agency for Research on Cancer (IARC) [64] and the U.S. Environmental Protection Agency (USEPA) [65, 66]. Several organizations, including the ATSDR, IARC, DHHS (the Department of Health and Human Services), OSHA (National Occupation Safety and Health Administration), and the USEPA has classified PAHs as carcinogenic compound. Table 2.1 shows the carcinogenic classification of 16 priority PAHs as per IARC, DHHS and the USEPA.

The Risk assessment of 16 PAHs was evaluated by using toxic equivalency factor (TEF) by many researchers in surface soil around the world [7, 67, 68, 69, 70, 71, 72]. In India evaluation of the PAHs toxicity along roadside soil within a fast developing northern city results that toxic equivalent factor of BaP and DaA were in higher side as compared to the other PAHs [73]. Thus BaP and DaA were the two most toxic and carcinogenic PAHs in the study area. The toxic potential of PAHs in traffic soil of Delhi, India was measured and found the average BaP_{eq} concentration in the traffic soil was 1009 µg BaP_{eq} kg⁻¹, which was a ~21 time higher than in the rural soils [29]. Sing et al. [33] also reported BaP_{eq} concentration of PAHs load in industrial and roadside soils, which were ~10 and ~6 times greater than the agricultural soil of Delhi. Toxicity assessment was also employed to the urban soil of the Brahmaputra Valley, North eastern India and the results showed that total mean BaP_{eq} values were

309 ± 525, 116 ± 93 and 557 ± 828 ng BaP_{eq} g⁻¹ during monsoon, pre -monsoon and post -monsoon seasons respectively [34]. Risk of PAHs exposure for soil in Guwahati was detected to be high during the pre-monsoon season.

Table 2.3 Carcinogenic classification of 16 USEPA priority PAHs as per IARC, DHHS and US-EPA.

PAHs	EPA	IARC	DHHS
Acenaphthylene	Not classifiable		
Fluorene	Not classifiable	Not classifiable	
Phenanthrene	Not classifiable		
Anthracene	Not classifiable	Not classifiable	
Fluoranthene	Not classifiable	Not classifiable	
Pyrene	Not classifiable	Not classifiable	
Benz(a)anthracene	Probably Carcinogen	Probably Carcinogen	Animal Carcinogen
Chrysene	Probably Carcinogen	Not classifiable	
Benzo(b)fluoranthene	Probably Carcinogen	Possibly Carcinogen	Animal Carcinogen
Benzo(k)fluoranthene	Probably Carcinogen	Possibly Carcinogen	
Benzo(a)pyrene	Probably Carcinogen	Probably Carcinogen	Animal Carcinogen
Dibenz(ah)anthracene	Probably Carcinogen		Animal Carcinogen
Benzo(ghi)perylene	Not classifiable	Not classifiable	
Ideno(1,2,3-cd)pyrene	Probably Carcinogen	Possibly Carcinogen	Animal Carcinogen
Fluorene	Not classifiable	Not classifiable	
Phenanthrene	Not classifiable		

Toxic equivalency factor was evaluated in groundwater samples at commercial site of Gorakhpur, India during winter season [41]. Results showed that IcdP contributed the highest carcinogenic exposure equivalent (0.32 ng l⁻¹) followed by BaP (0.30 ng l⁻¹), BbF (0.25 ng l⁻¹) and BkF (0.15 ng l⁻¹), accounting for approximately 28, 27, 22 and 13% of the total BaP_{eq} concentration of groundwater PAHs in this region, respectively.

2.6 Analytical Techniques

2.6.1 PAHs extraction

The extraction is considered as the most important step in the determination of PAHs in different environmental matrices since these hydrophobic compounds are strongly sorbed. The degree of extraction yield depends on the method used and especially on the type of solvent. Solvents like dichloromethane (DCM), hexane, DCM/acetone, hexane/DCM, toluene used in different extraction procedures.

2.6.1.1 Extraction of soil

The extraction of PAHs from solid matrix such as soil can be accomplished with conventional extraction techniques such as soxhlet extraction [47, 48, 56, 74, 75, 76, 77], ultrasonic shaking apparatus [78] and ultra-sonication [28, 29, 33, 79, 80].

In recent years, other extraction techniques have been studied to reduce the consumption of organic solvent, improve the precision of analyte recoveries and reduce extraction time and sample preparation. These modern technique includes accelerated solvent extraction (ASE) [49, 81, 82], pressurized fluid extraction [83], supercritical fluid extraction (SFE) [84, 85], microwave-assisted extraction (MAE) [86, 87], pressurized hot water extraction (PHWE) [88, 89] pressurized liquid extraction (PLE) [90].

Zuazagoitia et al. [91] compared two different headspace solid-phase microextraction (HS-SPME) for extraction of soil PAHs results the hot water direct HS-SPME was significantly superior to the sonication organic extraction-HS-SPME for screening method of PAHs determination.

2.6.1.2 Extraction of water

Extraction of PAHs from aqueous medium can be achieved by several methods such as liquid/ liquid extraction [15, 22, 41, 50, 92, 93], Solid Phase Extraction (SPE) [94, 95], Solid Phase Micro Extraction (SPME) [96] or Stir Bar Sorptive Extraction (SBSE) [97, 98].

2.6.2 Clean up

Column chromatography is commonly used for adsorption of the interfering substances in the extracted samples for PAHs purification. Some of the sorbents used in column chromatography includes alumina [47], silica/alumina (1:1) [58, 99] and the most widely used one is silica gel [28, 29, 76, 79, 82, 100]. In current times conventional chromatographic columns are replaced by pre packed commercial cartridges which are more advantageous in terms of time, solvents consumed and reproducibility of performance [101].

2.6.3 Quantification of PAHs

Day by day, tremendous improvements in analytical instrumentation have been occurring for better detection of the persistent organic pollutants. Many analytical techniques have been developed for the estimation of PAHs in different environmental matrix. The most common instrument used at present for identification and quantification of PAHs are GC/MS (Gas Chromatography/ Mass Spectrometry) [47, 49, 75, 76, 77, 99, 102], Gas chromatography together with Flame Ionization Detector (GC-FID) [21, 32, 51], HPLC (High Performance Liquid Chromatography) equipped with UV detector [28, 29, 53, 79], HPLC with a photodiode array detector [103], HPLC equipped with fluorescence detector [15, 78, 100, 104].

2.7 PAHs source apportionment

Several methods have been described in the literature for qualitative and quantitative assessment of PAHs sources in different environmental matrix. Some of these methods include the use of source diagnostic ratios [9, 105], Principal Component Analysis (PCA) [106, 107], Multiple Linear Regression (MLR) [103, 108], Hierarchical Cluster Analysis (HCA) [109, 110], Chemical Mass Balance (CMB) [111], Positive Matrix Factorization (PMF) [46, 112], UNMIX [113, 114].

2.7.1 Diagnostic ratios

The PAHs diagnostic ratios are important tools for the qualitative identification of pollution emission sources. Some diagnostic ratios are based on parent PAHs,

whereas, others on the proportions of alkyl-substituted to non-substituted molecules [115]. In order to decrease various challenging factors such as differences in volatility, water solubility, adsorption, computation of PAHs ratios are generally limited to PAHs within a given molecular mass [116]. However, several researchers have criticized the unquestioning application of PAHs diagnostic ratios [117, 118, 119].

The PAHs diagnostic ratios express intra source variability, but inter-source similarity [117]. The diagnostic ratios calculated for each proposed source may not be definitive. As per the diagnostic ratios reported by Ravindra et al. [120, 121], $IP/(IP+BgP)=0.37$ indicates diesel emission, whereas Kavouras et al. [122] described $IP/(IP+BgP)$ ratio range from 0.35-0.70 for diesel emission. Thus it is difficult to identify a particular source based on one particular diagnostic ratio. Therefore, use of multiple ratios validates the source apportionment study to a certain level. Table 2.2 describes the specific values of PAHs diagnostic ratios for a particular source category.

Table 2.4 Values of PAHs diagnostic ratios for a particular source category.

PAHs ratio	Value range	Source	Reference
Ant/(Ant + Phe)	<0.1	Petrogenic	[123]
	>0.1	Pyrogenic	[105]
Phe/Ant	<10	Pyrogenic	[124]
	>15	Petrogenic	[105]
Phe/(Phe+Ant)	>0.7	Fossil fuel burning	[122]
	<0.7	Biomass burning	
BaA/(BaA + Chr)	<0.2	Petrogenic	[105]
	0.2-0.35	Petroleum combustion	
	>0.35	Coal, grass, wood combustion	
	>0.35	Combustion	[125]
	0.5	Diesel	[126]
	0.73	Gasoline	
Fla/(Fla + Pyr)	0.60-0.70	Diesel vehicles	[127]
	0.43	Diesel vehicles	[128]
	0.62	Oil burning	
	0.42-0.52	Road dust	

	>0.5	Pyrogenic	[105]
	<0.5	Petrogenic	
Flu/(Flu + Pyr)	<0.4	Petrol emissions	[120, 121]
	0.4-0.5	Liquid fossil fuel combustion	[129]
	>0.5	Biomass and Coal combustion	
Flu/Pyr	>1	Pyrogenic	[124]
	<1	Petrogenic	
IcdP/(IcdP + BgP)	<0.2	Petrogenic	[105]
	0.2-0.5	Petroleum combustion	
	>0.5	Grass, wood and coal combustion	
	0.35-0.70	Diesel emission	[122]
	0.37	Diesel emission	[120]
Σ LMW/ Σ HMW	<1	Pyrogenic	[130]
	>1	Petrogenic	
Σ COMB*/ Σ PAHs	~1	Combustion	[121]
	0.78	Diesel vehicle	[131]
	0.73	Catalyst equipped cars	
	0.82-0.87	Wood combustion, Road dust	
BbF/BkF	2.5-2.9	Aluminium smelter emissions	[115] [132]
	>0.5	Diesel	
BaP/BgP	<0.6	Non-traffic emissions	[118]
	>0.6	Traffic emissions	
	0.5-0.6	Traffic	[133]
Nap/Phe	<<1	Petrogenic	[134]
IcdP/BgP	0.4	Gasoline	[135]
	1	Diesel	[29]

* Σ COMB= Fluorene+ Pyrene+ Benzo(a)anthracene+ Chrysene+ Benzo(b)fluoranthene+ Benzo(k)fluoranthene+ Benzo(a)pyrene+ benzo(ghi) perylene+ Indeno (1,2,3-c,d) pyrene.

Molecular indices based on ratios of selected PAHs concentrations are widely used to identify PAHs from petrogenic and pyrogenic origins in surface soil [105, 119, 123, 136]. The PAHs isomer pair ratios of Phe/ (Phe + Ant), BaA/ (BaA + Chr), Flu/ (Flu + Pyr) and IcdP/ (IcdP + BaP) were used to distinguish between petrogenic and pyrogenic sources in urban soil of Shanghai, China [31]. The data from the study indicated that the PAHs in Shanghai urban soil were mainly derived from combustion sources i.e pyrogenic (e.g. petroleum, biomass, coal). Source apportionment by diagnostic ratios such as Phe/Ant and Flu/Pyr indicated the strong pyrogenic influence on soil PAHs, specifically in industrial areas in top soil at Ji'nan city, China [76]. The isomer ratios of Ant/(Ant + Phe), Fla/(Fla + Pyr), BaA/(BaA +Chr), and IcdP/(IcdP + BgP) along with ratio of LMW/HMW PAHs showed that the PAHs in soils from the mid-southern part of the YRD were mainly derived from the petroleum sources; while in the remainder of YRD area, showed mixed sources of petroleum combustion and coal and biomass combustion [7].

In India, source apportionment study was undertaken by Ray et al. [28] to determine the sources of 16PAHs in the peripheral soil of the International Airport; Delhi using diagnostic ratios inferred that the primary source of PAHs in the study area was petroleum combustion. Interpretation of Ant/(Ant+Phe), Flu/(Flu+Pyr), BaA/(BaA+Chr), Flu+Pyr and BaP/(BaP+Chr) ratios implied that mixed pyrogenic activities such as biomass and coal combustion, petroleum combustion are the main sources of PAHs pollution in roadside surface soil of Delhi [137]. The study commenced by Bhupander et al. [138] conducted in urban roadside soil of India showed that fuel combustions occur in the vehicles was the major source of PAHs by using isomer ratio of Flu/(Flu+Pyr), IcdP/(IcdP+BgP), BaP/BgP, BaA/(BaA+Chr) and BaP/(BaP+Chr). Study conducted on urban surface soil of Brahmaputra Valley, [139] using isomer ratio Phe/(Phe+Ant), Ant/(Ant+Phe), Flu/(Flu+Pyr), BaA/Chr and IcdP/(IcdP+BgP) showed pyrogenic emission mainly from fossil fuel or gasoline and diesel type. The results of ratios like Ant/(Ant+Phe), Fla/(Fla+Pyr), BaA/(BaA +Chr), and IcdP/(IcdP+BgP) indicated that PAHs contamination in Dhanbad City was mainly due to vehicular emission with moderate effect of coal and biomass combustion [39].

The application of Phe/Ant, Flu/Pyr, Flu/(Flu+Pyr) and IcdP/ (IcdP+BgP) to oilfield soil of China showed petrogenic origin of PAHs sources of the samples near oilfield,

whereas the other sampling sites PAHs originates from combustion of petroleum. Analysis of Flu/Pyr ratio in peripheral soil of Zhongyuan oilfield, China indicated both pyrogenic and petrogenic input in terms of sources of PAHs [42]. Similar results were also obtained from the diagnostic ratio analysis in surface soil samples from oil exploration area of Nigeria Delta, Nigeria [140]. Abbas and Brack [47] investigated the origin of PAHs in oilfield surface soil of Nigeria Delta, Nigeria by applying five diagnostic ratio viz. Phe/Ant, Flu/Pyr, BaA/BaP, Pyr/BaP and Nap/ Phe. The ratios confirmed that both pyrogenic inputs like vehicular exhaust and heavy industry emission and petrogenic inputs were dominant source of PAHs in Nigeria soil. Use of ratios Phe/Ant, Fla/Pyr, Fla/(Fla+Pyr) and BaA /Chr indicated the presence of both petrogenic and pyrogenic sources of PAHs at two spilled sites of Calabar, Nigeria [49].

In aquatic environment the PAHs exists, suffer from photolysis [141], which could change the values of diagnostic ratios. Results from PAHs cross-plots for Ant/Phe against Fla/Pyr indicated that the PAHs contamination in water samples from YRD was most likely from mixed sources of petroleum and combustion [142]. Molecular ratios of Flu/(Flu+ Pyr) and Ant/(Ant+Phe) showed that in most of the drinking water resources PAHs were originated from combustion of wood and coal i.e. of pyrogenic origin in China [18]. A study was conducted by Riccardi et al.[143] on the influence of accidental fuel leaks from a tank on the groundwater system. The values of isomer pair ratio, Ant/(Ant/ Phe) and Flu/(Pyr/ Flu) proposed that PAHs present in groundwater originated from fuel leaks, nevertheless the pyrogenic origin of PAHs in some samples was also prominent. Analysis of surface water of Hangzhou city, China indicated that petrogenic (Flu/Pyr <1) input was mostly responsible for PAHs contamination of surface water [144]. Hussain et al. [139] investigated PAHs sources in surface water of Bharalu Tributary of Brahmaputra River using diagnostic ratio which showed considerable input of PAHs from combustion sources with some moderate input from petrogenic sources.

2.7.2 Principle component analysis/ Multiple Linear Regression (PCA/MLR)

The PAHs diagnostic ratios could only provide qualitative information about the contribution of various sources. Multivariate statistical tool like PCA-MLR was

applied to assume PAHs groups. The main purpose of this technique is the reduction of number of variables while holding the original information as much as possible and thus variables with similar characteristics can be grouped into factors [145]. Several authors [31, 146, 147, 148, 149, 150, 151] have reported the application of PCA/MLR to apportion the percentage contributions of major sources of PAHs in various environmental compartments. Source apportionment by PCA/MLR model in surface soils of Baise, China showed that coal and wood combustion, petroleum combustion and evaporative and uncombusted petroleum contributed over 52.1, 32.5 and 15.4% of the total source of soil PAHs, respectively [9]. Another study from Indonesia reported that three sources contributed to the PAHs in the study area, including biomass and coal combustion (48.46%), raw coal (35.49%), and vehicular emission (16.05%) [10]. Mean source contributions were found to be 25.45 % from diesel + coal and wood combustion, 11.45% from diesel + coal combustion, 6.97 % from traffic, 1.41% from vehicular and 54.72% from diesel engine vehicular emission as per a study conducted on surface soil of Brahmaputra valley [34]. In traffic soil of Delhi, PCA provided the fingerprints of vehicular traffic emission and coal combustion [29].

2.8 Relationship of PAHs-OC-BC

The soil TOC has been considered as a key property and governing factor for distribution, sorption, sequestration and fate of POPs [74]. Association of BC with PAHs in soils may be expected due to i) co-emission of BC and PAHs, ii) PAHs gas-to-BC particle partitioning during atmospheric transport, iii) PAHs air-to-BC soil partitioning and iv) Sorption of PAHs to BC in the soil after deposition.

Association of PAHs with TOC and BC was determined in soil samples from background locations of UK and Norway [56]. A significant statistical relationship was observed between PAHs and TOC in the Norwegian soil samples. In UK-woodland soil, HMWPAHs correlated with BC. These observations conclude that TOC plays an important role in retention of PAHs in soil and association of PAHs with BC during combustion emissions. Similar study was carried out by Agarwal and Bucheli [152] in the surface soils of Switzerland and Delhi, India. Both TOC and BC

revealed significant positive correlation with LMWPAHs, but not with the HMWPAHs in Swiss soils. In contrast, HMWPAHs were significantly correlated only with BC in Delhi soils. It appears that TOC governs the distribution of PAHs in organic matter rich background soils, whereas the association between BC and PAHs was reflected by closeness to emission sources in urban soils. Wang et al. [153] studied the correlation between PAHs and TOC in soils from Beijing, Tianjin and surrounding areas, North China during September 2007. They concluded that the LMWPAHs were more strongly correlated with the OC content in comparison to the HMWPAHs, mainly because of their higher saturated vapor pressure and consequently higher mobility. Ray et al. [154] investigated the relationship between PAHs and carbonaceous species in soil layer as the controlling factor of PAH pollution cycling. They reported that both BC and TOC are important geosorbents for PAHs and both of them, especially BC can be harnessed for sequestering PAHs by limiting their transport and retarding their bioavailability

On the other hand, pearson's correlation analysis performed by Liu et al. [103] at surface soil of Shanghai, China showed that the Σ PAHs in soils were not significantly correlated with TOC ($r = 0.062$ and $p = 0.65$). Jiang et al. [5] also reported a similar result between PAHs and TOC in urban soil of Shanghai. This may be due to non-equilibrium adsorption between TOC and PAHs in soils. Continuous input of fresh PAHs by vehicular and industrial sources is also one of the causes of such type of relationship. Accordingly, TOC may have less importance in controlling surface soil PAHs concentrations in such case [33].

2.9 Distributions of heavy metals

Metals are considered as the main inorganic constituents of environmental concern due to their toxicity and threat to human life and the environment. The "Heavy metals are the group of metals and metalloids having atomic density greater than 4000 kg m^{-3} , or 5 times more than water and they present naturally in the earth's crust [155]." The toxic influence of heavy metals on living organisms is indisputable. The mobility of the heavy metals in the ecosystems and their transfer in the food chains are the key issues in the environmental research on heavy metals [156, 157, 158, 159].

2.9.1 Heavy metal in surface soil

Heavy metals pollution in surface soil is a significant environmental problem worldwide [160]. Specifically, in many developing countries soil pollution with heavy metals due to extreme industrialization and urbanization has become a serious issue of concern [161, 162, 163, 164].

A total of 227 surface soil samples (0–0.1 m depth) from six different land use types were collected from Pearl River Delta (PRD) were analyzed for major heavy metals using microwave-assisted acid digestion and inductively coupled plasma–mass spectrometry (ICP-MS) [164]. The mean concentrations of Cr, Fe, Mn, Ni, and Pb in the soil samples were 67.2, 5,100, 371, 26.0, and 51.4 mg kg⁻¹, respectively. Soil pollution by Pb was more prevalent than the other heavy metals, which was mostly come from anthropogenic sources. On the other hand metals like Mn, Co, Fe, Cr, and Ni in the surface soils were mostly derived from lithogenic sources. Mean values of Cu, Ni, Pb and Zn were found to be 71.2±74.7, 22.2±8.7, 66.2±44.2 and 87.6±31.2 respectively in surface soil of urban park, Beijing, China [165] analyzed with a flame atomic absorption spectrometer. The investigation revealed that the accumulations of Cu and Pb were readily apparent in the soils. Analysis of PCA revealed that the source of Ni and Zn were parent material whereas Cu, Pd and a part of Zn were accounted from anthropogenic sources. The study revealed that the accumulation of Zn did not appear to reach pollution levels, and no obvious pollution by Ni was observed in the soils of the parks in Beijing. Similarly the multivariate statistical analysis showed that the metal like Cu, Zn, and Cd were associated with and controlled by anthropogenic activities in an agricultural area of China [166].

Researchers from India also did a lot of study on Heavy metal contamination of surface soil. Sharma et al. [167] investigated the heavy metal contamination of soil in suburban areas of Varanasi. The results showed that the mean concentrations in soil were below the Indian standards for all heavy metals, but higher value of Cd recorded during January. High level of metal was observed in soil samples near the industrial area, Rajasthan for metals like Pb (293 mg kg⁻¹), Cr (240 mg kg⁻¹), Cu (298 mg kg⁻¹), Zn (1,364 mg kg⁻¹) and V (377 mg kg⁻¹) [168]. The soils in the area require remediation as per environmental quality criteria. Also regular monitoring of toxic metals enrichment in the area needs to be carried out. Parth et al. [169] assessed the

heavy metal contamination in soil around hazardous waste disposal sites in Hyderabad city; found that the mean value of Cr and Pb concentrations exceed the threshold and natural background values, whereas the highest concentrations of Cu, Ni and Zn surpassed the prescribed threshold limit. Govil et al. [170] evaluated the spatial variability and extent of contamination in Patancheru industrial development area, Andhra Pradesh. The study reported that the soils in the area are significantly contaminated with two to three times higher levels of toxic elements than normal. Concentration of heavy metal such as Cr, V, Cd and Cu were 240, 235, 200 and 500 mg kg⁻¹ respectively. Most of the soils in the study area should be removed from agricultural production and the area needs to be monitored regularly for heavy metal enrichment.

Metal concentration in oilfield soil was also reported by various authors, considering oilfield as a possible source of pollution, since oil excavation activities raised the levels of metallic pollution (Cd, Cr, Ni, Cu, Zn, Pb and V) to the adjacent environment. Afkhami et al. [171] reported concentration of metals like Cr, Ni, Cu, Pb and Zn were far below the reference values however Cd and V are remarkably above the limits in Ahvaz oil field, southern Iran in October 2009. Edwin O. Adaikpoh [172] documented the existing status of some metals viz. Cr, Cu, Cd, Co, Ni, Zn, Pb, Mn and Fe as well as their bioavailability in surface soils of Umutu Oil Field, Niger Delta Nigeria using atomic absorption spectrophotometer. The study reported that except for the high contents of Cu, Cd, Co, Zn, and Pb in auto-mobile mechanic waste dumpsite, mean metal levels in mg kg⁻¹ are Cd (0.65-1.83), Cu (2.20-6.30), Pb (4.06-5.90), Cr (7.10-15.6), Ni (1.10-2.00), Zn (33.0- 45.0), Co (0.01- 0.06), Fe (1100- 3000) and Mn (1.83-18.8). Similar study was carried out in surface soils of another oilfield in the Niger Delta in two regimes, January – February, 2005 for dry season samples and June and July, 2005 for rainy season samples [173]. Soils around the gas plant showed higher concentration of metals viz. Cd, Pb, Cu; Ni, Zn, Cr and Mn than the pipeline areas. The heavy metals were distributed in soil by following order: Fe> Mn> Zn> V> Cr> Pb> Cu> Ni> Cd>. Comparing to the concentrations of metals in background levels and concentrations found in natural and agricultural soils and soil around the oilfield could be considered unpolluted. Xiao et al. [174] explored the impact of oil extraction on migration and temporal distribution of heavy metals namely Cd, Cu, Cr, Mn, Ni, Pb, V, Zn and Mn in soils of an oil region of Shengli

Oilfield, China. The mean concentrations of the measured heavy metals Cu, Zn, Pb, Cd, Cr, Ni and V were 18.4, 78.2, 20.8, 0.19, 56.6, 26.3 and 62.1 mg kg⁻¹, respectively. The vertical distributions of Cd, Cu, Ni, Pb, V and Zn were found to be affected in oil-polluted soils after comparing with the control profile, mostly those of Cd and Ni. Depending upon the duration of oil well development, the concentrations of Cd, Mn, Ni, V, and Zn in oil-polluted soils were augmented indicating the influence of anthropogenic activities. Potential sources of Cr, Ni, V and Cu in the soils were both natural sources and petroleum hydrocarbon spills, while Zn, Pb and Cd were probably from anthropogenic sources such as farming activities and traffic.

The total metal concentration and chemical fractionation of Cd, Cu, Cr, Ni, Pb and Zn in top soils around Lakwa oil field, Assam, India was studied during the period 1994–1995 [175]. Two to four fold increases in the metal concentration was observed after comparing it with the internationally accepted shale standard [176] and normal abundance values [177]. Concentrations of Cd, Cu, Ni, Zn and Cr were lower than the local background whereas, Pb and Co had higher values than the local background.

2.9.2 Heavy metal in groundwater

The harmful effect of toxic metals from contaminated drinking water has grown as one of the major threat to human health in the 21st century. Studies also confirm the heavy metal contamination of groundwater in many areas of India [178]. Current studies indicated that the levels of trace metals present in drinking water could seriously affect human health [179].

Impact of large-scale irrigation projects on groundwater status has been evaluated by Li et al. [180] in the North China Plain (NCP) on the basis of trace metal concentration. Concentrations of metals like Fe, Mn, and Zn in groundwater exceeded drinking water standards by 3.8, 11.5, and 7.7%. Combined origin of geogenic as well as agriculture and industrial activities were found to be the major source of these metals. Similar study was carried out in groundwater used for irrigation in Tabriz City's countryside in the end of spring and all of summer of 2010, the mean concentration of metal like Cd, Cu, Cr, Ni, Pb and Zn were found to be 6.55±3.80, 16.23±7.69, 3.41±1.90, 4.49±4.43, 0.79±1.65 and 49.33±42.61 µg l⁻¹ respectively [181]. The analyzed heavy metal concentrations, excluding Cd, were found below

allowable maximum level in potable water. Researchers from India also reported on metal contamination of groundwater. Ravishankar and Rao [182] evaluated the trace metals in industrial groundwater in and around Vijayawada, Andhra Pradesh and reported that Cd, Cr, Fe, Mn exceeded the maximum limits of WHO and IS10500 2012 for drinking water. The minimum and maximum trace metals concentrations in the study areas for, Pb, Cu, Fe, Ag, Zn, Cd, Mn, Ni, Cd, and Co are 0.012-0.153 , 0.00 and 1.85, 0.00 -1.35, 0.05- 0.20, 0.05 -1.5, 0.2-0.446, 0.081 - 0.155, 0.096-0.646, .007-0.137, 0.093-0.157 mg l⁻¹ respectively. Krishna et al. [183] reported the mean concentration of Cr, Mn, Fe, Ni, Zn and Pb were 16.8± 11.1, 72.9± 77.5, 162± 386, 26.7± 16.3, 98.6± 87.9 and 2.1± 3.0 respectively from industrial area of Andhra Pradesh. Source apportionment study concluded that Co, Ni and Cr were associated and controlled by mixed origin with similar contribution from anthropogenic and geogenic sources whereas Fe, Mn, Pb, Zn and Co were derived from anthropogenic activities. Concentration of Cd, Fe, Mn, Pb, and Zn were estimated in Brahmaputra flood plain of Barpeta District, Assam, India using atomic absorption spectrometer [184]. The concentration of Fe exceeds the WHO recommended levels in about 80% of the samples, Mn concentration in about 22.5% and Pb in about 22.5% of the samples. Cd was present only in four sites and three of them exceed the WHO permissible limit (0.003 mg/L). Concentrations of Zn were reported to be within the prescribed WHO limits. Similar study carried out in Kamrup district of Assam reported the concentration of Cu and Zn were within the prescribed WHO limits [185]. Significant positive correlation between Mn with Zn and Cu indicated their similar source of origin and mobility.

2.10 Analytical methods for determination of heavy metals

A number of analytical methods for determination of heavy metals in different environmental matrix are used in various studies. The most predominant techniques are Atomic Absorption Spectrometry (AAS) [166, 186]; Atomic Emission/Fluorescence Spectrometry (AES/AFS) [187, 188]; Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [164]; Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [189, 190]; Neutron Activation Analysis (NAA) [191], X-ray Fluorescence (XRF) [192] and Anodic Stripping Voltammetry (AVS) [193].

2.11 Application of pollution indices in metal toxicity studies

Different pollution indices like, Pollution Index (PI), Pollution Load Index (PLI), Nemerow Integrated Pollution Index (NIPI), Ecological risk factor (E_r^i) and potential ecological Risk Index (RI) were widely used to measure contamination level of heavy metals in surface soil [164, 165]. Pollution index is commonly used to assess environmental quality. Nemerow integrated pollution index is the environmental quality index based on weighted multi-factors, which reflects the degree of soil pollution caused by various heavy metals [194]. Pollution load index signifies the number of times by which the heavy metal concentration in soil exceeds the background concentration and provides an indication of the overall level of heavy metal toxicity. Main purpose of ecological risk assessment is to find a fast and simple quantitative value on the possible ecological risk of a particular condition in a system.

2.12 Heavy metal and PAHs

Inorganic tracers like heavy metals (Cd, Cu, Cr, Fe, Ni, Mn, V, Zn) could be used with PAHs for source apportionment study to advance the process and to validate the results since both of them are co-emitted from similar sources like biomass burning, wood combustion, coal and petroleum combustion, vehicular traffic emission. Napier et al. [195] reported from a study in the UK environment that automobiles are the major sources of Cu, Zn and PAHs to the environment. They reflected the significance of automobiles as a continuing source of persistent pollutants in the environment. Brown et al. [196] conducted a study on sources of PAHs and heavy metals in urban stormwater runoff in Dunedin, New Zealand over 7 storm events from 1998 to 2000. They concluded that the road debris, in particular street dust and tanker effluent solids were the principal sources of the heavy metals and PAHs in the storm water collected from New Zealand.

In Indian perspective few such studies has been conducted which reported the similar source of origin of PAHs and heavy metals. Association of PAHs and metallic species in a tropical urban atmosphere Delhi, India was characterized during December 2008-November 2009 with respect to 16 US EPA PAHs and 8 major and trace metals (Fe, Mn, Cd, Cu, Ni, Pb, Zn and Cr) [151]. PCA-MLR apportioned four common sources

viz. crustal dust (73%), vehicular emission (21%), coal combustion (4%) and industrial emission (2%) that was further validated by hierarchical cluster analysis (HCA). Temporal trend analysis showed that crustal sources were predominant in summer while the remaining sources were most active in winter. Particulate-bound PAHs and trace metals composition were determined at a site in Delhi (India) during the winter and summer periods in 2007–2008 by Singh et al. [197]. The results of diagnostic ratio and enrichment factor analyses showed that vehicular and anthropogenic emissions related to combustion, industrial processes as well as natural sources associated with the transport of dust from the roadside area were the main pollutant sources for PAHs and trace metals. The levels and distribution patterns of $\Sigma 16$ PAH and heavy metals (Pb, Cu, Ni, Co and Cr) were determined in soil in the vicinity (5 km radius) of an oil refinery in India [198]. Concentration of $\Sigma 16$ PAH in the soils was found to be 60.4 mg kg^{-1} . The levels of Pb, Cu, Ni, Co and Cr in soil were 12.5, 13.5, 18.8, 4.84, and 8.29 mg kg^{-1} . Molecular diagnostics indices of PAH (Ratio of Phe/Ant, Flu/Pyr) indicated that the oil refinery environment was contaminated with PAH from petrogenic as well as pyrolytic origin and heavy vehicular traffic on the Agra- Delhi National highway. A comprehensive assessment of USEPA's priority 16 PAHs and heavy metals in street dust of Guwahati, a fast growing city of the Brahmaputra Valley was carried out during 3 seasons viz. monsoon, post-monsoon and pre-monsoon of 2011-12 [199]. In the study PCA, diagnostic ratios and correlations of PAHs with heavy metal implied that the PAHs originated mainly from coal and wood burning, and vehicular emission sources along with the metal species. To study the impact of automobile and industrial emission, distribution patterns of 16 different PAHs and 8 heavy metals were investigated in the soil samples collected from 15 different sites in Guwahati, Assam [200]. Higher concentration of total PAHs and heavy metals was found in the industrial areas compared to the high traffic areas. Differences in the pollutants observed between the polluted and nonpolluted sites, endorse that anthropogenic activities are the major cause of soil contamination by PAHs and heavy metals.

The spatial distribution of 16 PAHs and 8 heavy metals (Pb, Cu, Ni, Cd, Zn, Fe, Mn and Cr) were studied in 10 crude oil contaminated sites of Assam, India as PAHs are considered as an essential component of heavy metal and both are coexist with crude oil. [201]. The $\Sigma 16$ PAHs in soil were detected with a minimum of 13.48 and a

maximum of 86.3 mkg^{-1} and $\Sigma 8$ heavy metal concentrations in the soil ranged between 69.5 and 336 mg kg^{-1} . A negative correlation was detected between the relative concentrations of PAHs and metals. The results confirmed that the non-biodegradable nature of heavy metals made them stay in the soil for longer periods of time.

Thus, this can be regarded as another important aspect for the researchers during the study of PAHs source apportionment. The synchronized buildup of heavy metals and PAHs have gained considerable attention from the researchers since soils polluted with PAHs were often reported to contain high quantities of heavy metal [202, 203].

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