Chapter 2
Review of Literature
2.1 Worldwide Scenario of PAHs

2.1.1 Atmospheric Deposition of PAHs in all Environmental Matrices Worldwide

PAHs have been extensively studied. For most of the developed countries, background levels of PAHs are available. Researchers from different parts of the world have reported several studies on atmospheric deposition of PAHs for last three to four decades.

Among earlier studies, Lunde et al. [221] performed study on organic micro pollutants in precipitation in Norway. Snow and rain samples were collected and analyzed for 4 chemical groups namely alkanes, polycyclic aromatic hydrocarbons, phthalic acid esters and fatty acid ethylesters. Both particle adsorbed and water dissolved phase organic components were fractionated for analysis. They reported presence of alkanes and PAHs in precipitation samples and considered fossil fuel to contribute these organic micro pollutants in precipitation.

Noort et al. [222] determined the temporal variation of PAHs concentration in rain during three precipitation events. The rain samples were collected simultaneously at ground level and at an altitude of 200m. The concentration of Phen and Flan was remarkably higher in former than that of later as reported in the study. The presence of Phen was considered to be result of below-cloud gas-phase scavenging. The range of studied PAHs was BDL to 110 ng/l.

To estimate PAHs fluxes [223] within the Lake Michigan basin to coastal waters adjacent to the Chicago urban area and found that dry deposition loading for PAHs were three times higher than that of wet deposition.

Polkowska et al. [6] estimated PAHs in atmospheric precipitation including rain and snow in Poland. Phen, Flan and Pyr were the dominant PAHs in precipitation samples. Seasonal attributes were recognised in both rain and snow with maximum PAHs concentrations during winter which was attributed by them to be primarily from
residential heating. Another significant PAHs source was identified as traffic emission by them.

Bulk deposition and gas exchange of PAHs were estimated in the Galveston Bay, Texas by Park et al. [224] and reported atmospheric PAHs in vapour phase and in the rain dissolved phases. They had found Phen and Naph to be the dominant individual PAHs in air vapour and rain dissolved phases. Particulate phase of both air and rain samples were found to be dominated by 5and 6-ring PAHs. Moreover, air to surface water gas exchange was recognized as principal deposition process for PAHs compare to wet deposition. Combustion and petroleum deposition were identified as major sources of PAHs in the studied area. Levels of PAHs in bulk (wet and dry) precipitation were conducted by Manoli et al. [78] in the main plain of central Macedonia in Northern Greece. They observed maximum PAHs concentration during cold months. For deposition flux, the greatest values were revealed during large precipitation events coinciding with high PAHs concentrations. PAHs in bulk deposition were found to influence that of surface water as their signatures showed strong association.

In an urban region of Poland, Grynkiewicz et al. [119] estimated 16 PAHs in bulk precipitation (dissolved in water and adsorbed on solid particles) in which compounds were recovered using solid phase extraction method and analysed in GC-MS. In this study Naph, Phen+Anth, Flan and Pyr were found to be dominant compounds with high concentration values. On the other hand, trace level of Acy, Acen, Flu, BbF+BkF, IP, BaA and BgP were also reported. High PAHs concentration in winter samples and major contribution of coal fed heating to average PAHs load was observed. Vehicular traffic was identified to be a major source of total PAHs in precipitation.

Similar method of PAHs estimation was adopted by Golomb et al. [113] while determining wet and dry deposition of PAHs near New England coastal water. In this study wet (rain and snow) samples were received into a shielded, temperature controlled collecting bottle and an exposed water surface was used as a collector for gaseous and particulate dry PAHs deposits. High wet and dry deposition was observed during heating season. It was also reported that precipitation during non-convective events brought more wet deposition of PAHs than convective events. In this study chemical mass balance (CMB) model was used for apportionment of sources and identified diesel and gasoline fuelled vehicle and wood burning as major sources of PAHs.
Seasonal variation of PAHs in atmospheric precipitation in a rural site of Lake Balaton, Hungary was examined [225] and higher level of 3-6 ring PAHs was observed during the winter (3-350ng/l) than during the summer (1-54ng/l) with highest wet deposition rate of 412 µgm^{-2}year^{-1}. The most abundant compounds in snow samples reported by the group were Phen, Flan and Pyr.

Atmospheric bulk deposition PAHs was also studied by Ollivon et al. [118] during 1999-2000 in Paris, France. High abundance of Flan and Pyr was observed in bulk deposition samples by them. Vivid seasonal variation was observed with the highest concentration during winter. Temperature was found to play an important role in scavenging of LMWPAHs. The heating contributed 41\% to the overall annual PAH load. In other study Montelay-Massei et al. [115] estimated PAHs in bulk deposition during 2001-2002 on weekly basis at Evereux, West of Paris (France). Similar trends were reported and dominant Phen, Flan and Pyr were the species contributing 69\% of total PAHs. Moreover, LMW PAHs were found to correlate well with high rainfall. Principal Component Analysis (PCA) was used to identify meteorological influence as well as seasonal variability in that study.

Bulk deposition of PAHs at remote, rural village and an urban area of Beijing-Tianjin, North China were studied during 2007-2008 [123]. High deposition flux of Phen (35.3\%) and Flan (25.7\%) were observed. Highest deposition during fall was estimated which indicate high exposure risk during this season. Spatially, urban areas (8.28µg/m^{2}/day) received high deposition flux than that of rural ones (3.91 µg/m^{2}/day).

PAHs flux in various environmental compartments viz. ambient air, atmospheric deposition, soils, sediments, runoff and surface waters was monitored in Seine estuary, France to identify the major pathways of transport and accumulation through a mass balance model. Transport of PAHs from the atmosphere to watershed outlet was investigated for two rural and urban experimental watersheds within the Seine Estuary. High loading for atmospheric input of PAHs was observed in rural areas relative to urban areas, where atmospheric loading was found to be negligible [63].

Yan et al. [226] conducted a large-scale survey on distribution and deposition flux of PAHs in rainwater samples in Shanghai, China and reported annual deposition flux of PAHs was found to be 4148 kg/yr in collected samples. Naph, Phen, Anth and
Flan were revealed as the most dominant PAHs in rainwater. Along with diagnostic ratios together with back trajectory analysis was also performed by them to identify the pollutant sources. Combustion of grass, wood and coal were suggested to be major contributors of PAHs in that study. Air mass from Southern part of China was observed to enrich PAHs in Shanghai.

2.1.2 PAHs in Soil

Study of PAHs in soil has been performed extensively from various part of the globe. Some Researchers also tried to estimate atmospheric signature in soil and vice-versa.

Aamot et al. [227] investigated levels of nine selected PAHs in surface soils from southern and central Norway. Concentration in southern Norway was observed to be higher than that of central Norway in general; which was approximately ten times higher in case of 4 and 5-ring PAHs. Atmospheric transport was found as major contributor source of PAHs in soil after comparing with air quality data in south Norway. Atmospheric signature in soil was confirmed with the analysis of peat cores from ombrotrophic bogs, which is considered as a potential approach to assess temporal variation of atmospheric PAH deposition. Naphthalene concentration in soil was found to be very high compared to many other studies. Similar study was carried out in seven locations across the Seine River basin, France was estimated by Montelay-Massei et al. [228]. They observed distinct spatial variation with concentration industrial and urban areas to be in order of magnitude higher than those at the remote areas. High percentage contributions of carcinogenic PAHs (approximately 40%) were reported. This study also highlights the potential use of soil sampling to estimate spatial differences in atmospheric inputs of PAHs based on differences in regional and local atmospheric emissions.

Association of PAH with total organic carbon (TOC) was observed for Norwegian soil samples [229]. In UK-woodland soil HMWPAHs found to be correlated with black carbon (BC) which was considered as PAHs from combustion source. Four and more ring PAHs were found to be dominant in the UK soil than that of Norwegian soil. The PAHs profile was regarded as indicator of fractionation that occurred during long-range atmospheric transport and deposition. Thus the LMWPAHs with
lower $K_{ow}$ values were found to be more susceptible to reach the most remote sites, whereas the HMWPAHs with higher $K_{ow}$ values retained near to emission sources.

Spatial distribution and sources of PAHs in soil of Valasske Mezirici was investigated by Plachá et al. [230]. PAHs concentration in urban, agriculture and forest soil were analysed and found to be maximum at high altitude forest soil. The maximum PAH level was found to be higher than that of the forest soil in Western and Northern Europe. Meteorological condition with frequent calm condition associated with inversion state was considered as major contributing factor for such high PAH concentration at the high altitude forest. Industrial processes, transport and local heating activities were identified as significant source of PAHs in soil.

Wang et al. [231] reported air–soil gas exchange flux in Beijing–Tianjin region, North China with annual median PAHs flux of 42.2 ng/m$^2$/day from soil to air. Acy and Acen were observed as major contributor in total exchange flux. The air–soil gas exchange fluxes of PAHs were higher at the urban sites than those at the remote and rural sites. Seasonal variation also found to affect the mechanism with more gaseous PAHs volatilized from soil to air in summer with rise of temperature and increased rainfall. However, more gaseous PAHs were recognised to be deposited from atmosphere to soil during winter because of higher PAH emissions and lower temperature. The air–soil gas exchange of PAHs was not found to be influenced by TOC concentration.

**2.1.3 PAHs in Street Dust**

As compared to air and soil, street dusts have been a newer matrix in terms of studies relative with PAHs.

Among the earlier studies Takada et al. [145] reported molecular distributions of PAHs in street dust samples in Tokyo. Level of total PAHs concentration was found to be a few micrograms per gram of dust. Individually, 3- and 4-ring PAHs such as Phen, Flan and Pyr were recognised as dominant ones in the street dust. It was observed that automobile exhausts were the major source of PAHs in streets with high traffic density, whereas in residential area stationary sources of heating were identified as significant source. Pengchai et al. [232] also studied PAHs profile in urban road dust in Tokyo. This study mainly aimed to explore source identification of PAHs in road dust using cluster
analysis combined with PCA. Seven categories of PAHs sources were recognised including diesel and gasoline vehicle exhaust, vehicle exhaust, tire, asphalt or bitumen, asphalt-pavement, petroleum products and the combustion products except for those in vehicle engines.

Seasonal variation in street dust was reported by Netto et al. [233] in the center of Niteroi, a tropical city located in the State of Rio de Janeiro, Brazil, at the margins of Guanabara Bay. The maximum PAH concentrations were found in the month of July when the temperature was minimum. Individually, maximum geometric mean was detected in case of Pyr, Flan and Naph. Carcinogenic PAHs contribution was found to vary from 29 to 45%. PAHs showed significant correlations with daily mean and minimum temperature, as well as the overall temperature during sampling period. This indicate that meteorological parameter mainly temperature play an important role in PAHs distribution in street dust.

Liu et al. [234] performed study of PAHs in road dust samples collected from central Shanghai during winter and summer. Seasonal variation was reported with higher level of total PAHs during winter than that of summer. Moreover, spatial variation was observed with high concentration levels at industrial site, traffic site and commercial sites during both the seasons. HMWPAHs were found to be dominated in all areas. Mix source of traffic and coal combustion was identified for road dust PAHs using PCA. Pyrogenic and petrogenic source contribution were 71.0% and 11.4% respectively during winter, while 64.9% and 14.1% respectively during summer.

Samimi et al. [160] investigated PAHs contamination level in the form of settle dust in different types of samples including street dust, soil and water of a western highway in Tehran, Iran. Very high PAHs contamination was observed in the vicinity of the highway. Naph and phen were found as most common individual PAH in all the samples. The presence of these compounds was an indication of emission from incomplete combustion of vehicular fuels and their subsequent adsorption to atmospheric suspended particles which were finally settled in surface of street dust, soil and water near to highway.
2.1.4 PAHs in River Water and Sediment

PAHs behave in a very complex manner in aquatic environment. More so, natural water bodies often act as sink of PAHs from both atmosphere and terrestrial runoff. Biological risk is also directly associated with aquatic environment. All these facts usher researchers to get more interest in aquatic environment.

Smith et al. [235] measured PAHs in waters from three rivers which flow through the largest cities in south-eastern Australia. Smaller ring compounds were found to be more abundant with higher concentration than the larger ring ones in this study.

Skrbić et al. [236] estimated PAHs in the surface soil samples of Novi Sad city and bank sediment of Danube covering entire city and found that total PAHs content in bank sediments were higher than that of surface soil. Overall percentage contribution of BaP was found to be 6-14% of the total PAHs. The total carcinogenic potency for most of the sites was observed to be on higher side than recommended levels.

Spatial distribution of PAHs in surface water, suspended particulate matter (SPM) and sediment of Daliao River watershed composed of the Hun River, Taizi River, and Daliao River was investigated by Guo et al. [237]. Both diagnostic ratio and PCA was employed for source identification. Composition of PAHs was found to be dominated by 4-6 ring PAHs in the entire three medium. High occurrence of LMWPAH in water and SPM was recommended for recent local source and atmospheric deposition. High pollution load in water and sediment near industrial area indicated input from industrial wastewater.

To assess potential risk of PAHs from street dust to urban streams reflecting source-sink mechanism through stromwater Hongtao et al. [238] assessed PAHs in street dust particles and river sediments (Yangtze River Delta) in Xincheng, China. In street dust smaller particles found to have higher concentration. The sediments of the urban stream reaches in town were found to act as sinks for street dust PAHs. More so, total loads of PAHs in receiving water bodies is found to influenced by factors including particle size, land use and the hydrological conditions in the stream network as recommended by many researchers.
Major inputs and sources of PAHs into surface water, stream and precipitation along the Sacramento River, California was investigated by Kim and Young [239]. Concentration of total PAHs was found to be higher in surface water than precipitation, however, dissolved PAHs content in both the matrix was observed to be almost similar. Individually Naph, Phen, Pyr and BgP were identified as most dominant compounds in both surface water and rain. In dissolved phase more than 4-ring PAH compounds were rarely occurred. During wet season significant input of PAHs in surface water was observed through indirect deposition (i.e., washoff of atmospheric particles previously deposited to land) in California's Mediterranean climate. During wintertime although there was remarkable increase in aqueous PAHs level no apparent seasonal change was noticed in dissolved PAHs concentrations. Marker PAH ratios suggested pyrogenic origin of rainwater PAHs whereas complex and variable origin of PAHs were recognised in case of surface water.

Li et al. [240] investigated PAHs in soil, water, sediment, and plant samples collected from Aojiang River and its estuary. The concentration of PAHs in soil, water, sediment and plant were found to be relatively high while considering the population size of the area. Petrogenic sources were identified in sediment using diagnostic ratio. The composition profile of PAHs in soil and sediment was found to be similar with dominance of 4-6 ring PAHs.

Chemical analysis and biotoxicity was assessed by Fu et al. [241] to estimate the distribution, source, ecological risk and ecotoxicity of PAHs in sediments of Huaihe River. Diagnostic ratio revealed mainly pyrogenic origin of PAHs in the river sediment. Some of the individual PAHs were found to pose occasional biological risk, however no sample was identified for frequent biological impairment. However, some of the sites were observed with very high carcinogenic potential value.

Levels, dispersion patterns, seasonal variation, and sources of PAHs in Hun River of Liaoning Province, China was conducted by Zhang et al. [242]. The total PAHs concentrations were prominently elevated periodically in the order of level period > flood period > dry period. Dominance of LMWPAHs was noticed particularly for 2-3-ring PAHs. Predominance of LMWPAHs with high concentration during flood period was considered as relatively recent local source of PAHs. Selected PAHs ratio was used for source identification which indicated petrogenic origin of PAHs during dry season, while
mixed pyrogenic and petrogenic source during wet season. After comparing contamination level of PAH among different types of area it was prescribed that atmospheric deposition was the most important mechanism of PAHs entry into water system.

2.2 Indian Scenario of PAHs

While in many European countries studies on environmental PAHs initiated in the 1960s, most of the studies, on the similar lines, in India started in the early 1980s only. The preliminary studies were taken up with the cancer indicator BaP. The carcinogenic risks of BaP to people were studied in cities like Bombay (now Mumbai) and Ahmedabad. Later, with time, several groups from many parts of India started to study PAHs in various matrices including soil, sediment, water and atmospheric particulate matter.

2.2.1 Atmospheric PAHs

In comparison to other environmental matrices - soil, sediment and water - a good number of studies have been carried out on the atmospheric levels of PAHs in India so far. However, most of these studies were from major urban centres and their adjoining suburban and rural localities. Furthermore, source apportionment studies of PAHs from both urban and rural sites are also reported by several researchers.

Increasing incidence of lung cancer among various populations worldwide led to a growing concern among researchers about environmental carcinogens. Some PAHs like BaP for long been identified as a carcinogen and PAHs being ubiquitous in the environment, there is a tremendous increase in the studies on PAHs, especially BaP, were carried out in India in the last 3 decades.

In one of the pioneering study in India, BaP levels in air of general community, near domestic fire pots in kitchen and traffic junction in Ahmedabad were reported by Aggarwal et al. [243]. This study identified high BaP concentrations in urban conditions and opined that an association between urban-rural gradient of lung cancer incidences
and environmental BaP exposure could be traced for many other developing countries of Asia or Africa and, therefore, intensive studies are required to understand the relationship of BaP and lung cancer. During the same period of time and with similar analytical methods (TLC / spectrofluorometry), Mohan Rao et al. [244] reported BaP concentrations in atmospheric particulate matter of urban, suburban and rural region of Bombay and made attempts to find a possible correlation of BaP with lung cancer incidences among different populations. Wide spatial variations of BaP levels were observed by Mohan Rao et al. [244] and they opined that such variation could indicate suitability for epidemiological investigations.

Urban PAHs size distribution in gas/particle phase in Mumbai was studied and found to be regulated by both size-dependent adsorption and absorption to urban fine mode aerosols. Range of average PAHs concentration in aerosol in Indian Institute of Technology (IIT) Bombay and Regional Telecommunications Training Centre Saki Naka, Mumbai was found to be $2.1 \times 10^{-2}-4.2 \times 10^{-2}$ µg/m$^3$ [245]. They presented a very interesting finding on the adsorptive behavior of PAHs; predominance of non volatile PAHs in the fine mode and semi-volatile ones in the coarse mode.

Later, Kulkarni et al. [246] reported $\Sigma$PAHs concentration range of $2.45 \times 10^{-2}-3.88 \times 10^{-2}$ µg/m$^3$ in particulate matter of IIT, Bombay and Saki Naka, in Mumbai with a dominance of Pyr and BaP+Chry both the sites.

As concerns over PAHs grew, groups in lesser known cities like Bhilai, started assessments with respect to health risks. Pandey et al. [212] measured PAHs in the ambient air particulates in Bhilai industrial city and emphasized on the need for assessment of PAHs in the light of risk posed to human health.

Researchers at NEERI conducted a very early study from 1991-2005 to see the ambient air quality status for PAHs level of SPM and RSPM in 10 major cities of India. In this study the highest concentration range of 283.9-2113.6 µg/m$^3$ was found in Kolkata. Descending order of concentration range was Chennai (243.8-1481 µg/m$^3$) then Kanpur (197.4-2397.2 µg/m$^3$) then Mumbai (212.8-1402 µg/m$^3$) and then Delhi (186.9-1597.3 µg/m$^3$). So this can be concluded that Kolkata is the highest polluted metropolitan city in respect of PAHs [247].
Ambient PAHs were monitored in residential and industrial area of Delhi in 1998 during winter, summer and monsoon and this study was reported in CPCB [248]. The concentration of PAHs during winter, summer and monsoon was 30.3-60.9 ngm$^{-3}$, 16.0-29.3 ngm$^{-3}$ and 9.4-27.8 ngm$^{-3}$ respectively [249]. So, maximum PAHs level was observed in winter.

A pilot study was carried out to examine the PAHs profile in PM$_{10}$ in a residential site in New Delhi. The reported value in this study was also found to be comparable with that of TEERI [250] and also inferred that local source signatures are needed to get a complete picture of organic fractions of urban aerosols [251].

Simultaneous rain and air sampling was performed for thirteen rain event in Trombay, Mumbai during monsoon season in 2001. This study observed that with the increase of molecular weight the gas phase scavenging ratio of PAH also increased and for volatile PAHs the particle phase scavenging ratio values were found to be higher [252].

Suspended particulate matter samples were collected in Jawaharlal Nehru University Campus for PAHs analysis. Seasonal variation was investigated in the study and reported maximum concentration in winter and minimum during monsoon. Seasonality in source signatures was also revealed with major contribution from coal and wood combustion in winter samples. However, diesel and gasoline driven vehicles were identified as principal PAHs sources in atmospheric particulate matter throughout all seasons by using PCA [253].

Alternative fuel is the very way out for air quality improvement. Keeping this in mind Khillare et al. [254] investigated the comparative study of PAHs concentrations in PM$_{10}$ from three areas Daryaganj (DG), Moti Nagar (MN) and JNU in Delhi during Pre-CNG and Post-CNG period. This study revealed that use of alternative fuel could lead to 58-68% reduction of $\sum$PAH concentration.

Pandit et al. [255] carried out a study on PAHs in ambient air of creek area to investigate gas influx direction in air water interface. The study revealed active transfer of LMW dissolved PAHs into the atmosphere due to volatilization and deposition of HMW gas-phase PAHs into the surface water.
Levels of 3PAHs in the suspended particulate matter of an urbanised industrial site of India was monitored at two locations: the CISF building Sector 4, Bhilai, and the MPEB station at Bhilai-3, the twin city of Bhilai-Durg situated in the Mahanadi (Great River) basin of the Madhya Pradesh. Concentration range of BaA, BbF and BaP which are potentially weak and moderate carcinogens were BDL-1.56×10^{-1} µg/m³, BDL-1.28×10^{-1} µg/m³ and BDL-1.01×10^{-1} µg/m³ respectively in ambient air of Gwalior city, Madhya Pradesh (covering all Industrial, Commercial & Residential zones). Higher concentration was observed in winter at commercial areas & minimum at residential area. Enhancement in disintegration rate of organic compound in summer was the reported possible cause of such concentration trend [256].

PAHs in the suspended particulate matter and respirable suspended particulate matter were studied in airborne particulate matter in a petroleum refinery in west coast of India in six directions. A comparison of the PAHs concentrations showed that the average PAHs concentrations in major Indian cities were in the range of 5.81×10^{-1}–9.6925×10^{-1} µg/m³, which is less than the PAHs concentration of 10.92-100.82 µg/m³ around the refinery [257].

In Nunhai, an industrial site in Agra total PAHs concentration in TSPM from December 2005 to August 2006 was monitored. A relationship between PAH concentration and temperature was revealed where winter concentration of PAH was four-fold higher than summer. Higher fuel consumption coupled with lower mixing layer height, lower temperatures and less photodegradation were considered to be the possible cause of such high PAH level during cold periods [258]. Rajput et al. [259] conducted another similar study on PAHs in the same area from May 2006 to September 2006. The results indicated that PAHs concentrations were higher than many other industrial sites. Such higher concentration of PAHs revealed their higher emission rates in Nunhai as well as higher adsorption of gas phase PAHs by TSPM.

Masih et al. [260] measured PAHs in airborne particulate matter (PM_{10}) from four different sites of industrial, residential, roadside and agriculture area in Agra, amongst which industrial site recorded highest total PAHs concentration. The PAH concentrations in industrial (9.79×10^{-2} µg/m³), residential (3.46×10^{-2} µg/m³), and roadside (2.87×10^{-2} µg/m³) areas of Agra are less than the concentrations found in Taiwan (0.1101µg/m³) [industrial] [261] and 7.45×10^{-2} µg/m³ [residential] [261] and in Italy/Chile (5.48×10^{-2}
In the present study, the concentration of PAHs (8×10⁻³ µg/m³) in agricultural areas was found to be higher than in Malaysia/Taiwan (3×10⁻¹ - 5×10⁻¹ ng m⁻³). Another study in the same area for gaseous/particulate bound PAHs of outdoor rural environment was carried out. In this study the highest concentration was recorded during winter, lower in summer and lowest in rainy season [263].

In Ambathur, Kolathur, Saidapet, and Egmore representing urban, commercial, urban-residential, and industrial regions of Chennai PAHs in PM₂.₅ was measured and found higher than (National Ambient Air Quality Standard) NAAQS annual average of 1ng/m³ indicating an alarming pollution level in Chennai [264]. Singh et al. [265] monitored PAHs in PM₁₀ and PM₂.₅ at G.G.S.I.P University campus in eastern part of Delhi. This study found concentration of both PM₁₀ and PM₂.₅ higher than the prescribed limit of WHO and the NAAQ given by CPCB India. ∑PAH concentrations for PM₁₀ and PM₂.₅ were much higher in winter as compared to summer with predominance of 4-6 ring PAHs.

Gupta et al. [266] measured 4PAHs (Pyr, BaP, BgP and BbF) in ambient aerosol particles using a five-stage impactor at six different sites in Delhi for both the coarse and fine fractions. It has also been observed that the PAHs concentrations, in most of the cases, increase with decrease in the particle size, with lowest concentration in >10.9 µm size and highest in <0.7 µm.

PAHs in ambient respirable particles PM₁₀ from Jawaharlal Nehru University campus (JNU) in Delhi were recorded. Nearly 85% of the PAHs profile was dominated by combustion-derived large-ring compounds that were considered to be local in origin. In this study for the first time both organic and metallic characterisation in atmospheric particulate was conducted which revealed a better result for source apportionment [173].

A passive air sampling was carried out to estimate ambient PAHs in Imphal (urban), Thoubal (rural), and Waithou (mountain) of Manipur, Northeast India in the year 2009. The urban air was found to be most polluted compared to that of rural and mountain. The PAH profile was dominated by 2–3 rings PAHs. Seasonal variation was observed for PAHs with higher concentration during autumn and winter compared to spring and summer. Diagnostic ratio indicated sources of diesel and gasoline driven
vehicles in urban and mountain sites while coal burning in rural site PAHs. Sources of PAHs were identified to be both local and long range transport of southern Indian cities including Indian coastal regions and from Bangladesh [267].

2.2.2 Indoor PAHs

Biofuels, including wood, dried animal-dung cake and crop waste, are used extensively for cooking energy in India. High concentrations of PAHs in particulate have been reported in indoor environments, during biofuel combustion for cooking. In India, 70% of population depends on such biomass fuels for domestic cooking, and 78% of the population thrives on the biomass fuels in general [243, 268, 269-270].

Raiyani et al. [270] investigated indoor PAHs in kitchens with varied fuel type in Ahmedabad and found over 75% of the PAHs were in the particulate size bins of <2µm.

Pandit et al. [271] conducted a study on PAHs of Particulate matter in Trombay, Mumbai for indoor and outdoor of three houses where kerosene was used as cooking fuel. This study revealed significant indoor pollution due to use of kerosene as fuel. Moreover, mean concentrations of some individual PAH compounds were found with higher values by approximately an order of magnitude in indoor cooking environments than outdoor cooking environments with the effective total daily exposure was two times higher than that from ambient.

As cooking stoves using biofuel are high in use in Indian conditions, size-resolved emission factors of PAH from such cooking environment in India were measured using a dilution sampler. Emission factors of $\sum$PAH for wood, briquette and dung cake combustion were in the range of $2 \times 10^{-3}$ – $3.2 \times 10^{-3}$ mg/ g, $2.8 \times 10^{-3}$ – $3 \times 10^{-3}$ mg/ g and $3.1 \times 10^{-3}$ – $5.5 \times 10^{-3}$ mg/ g respectively for per mass of fuel burnt [272]. In a rural area of Lucknow in north India $\sum$PAHs in particle bound indoor cooking area was monitored. This study reported that the concentrations of carcinogenic PAHs were significantly high in breathing zone and in surrounding areas during cooking over chulha in rural India and was higher during winter than summer. PAHs concentrations were also increased considerably during biomass combustion. Thus the daily exposure to high concentrations of carcinogenic PAHs in indoor air environment could lead to chronic
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pulmonary illnesses in rural Indian women while cooking food [273]. Ansari et al. [269] conducted a study on PAH compounds in PM$_{2.5}$ and PM$_{10}$ from North India, Bithauli near Lucknow during cooking period and non-cooking period. The pollutant levels during cooking were significantly higher compared to the non-cooking period. This study also confirmed that indoor pollution depends on the kind of biomass fuel used for cooking. In Agra PAHs in kitchen, living room and in outdoors at urban site was recorded, where maximum concentration was found in Kitchen. But the high BaP concentration was detected in roadside living room (37.75±3.74) [260]. In this study, BaP level of kitchen in both roadside and urban areas were showing similar trend.

To prove the hypothesis that PAHs emissions differ with variance of biomass fuel used, Singh et al. [274] determined emission factors and emission estimates of PAH emitted from dung cake, fuelwood and crop residue from rural household of six states of Indo-Gangetic Plains in India including Delhi, Uttar Pradesh, Punjab, Haryana, Uttarakhand and Bihar. The average emission factors of total PAHs from dung cakes, fuelwood and crop residue are found to be 59.5 ± 19.9 mg kg$^{-1}$, 52.5 ± 19.6 mg kg$^{-1}$ and 40.9 ± 15.2 mg kg$^{-1}$ respectively. The emission factor of particulate phase PAHs (56.5 mg kg$^{-1}$, 45.3 mg kg$^{-1}$ and 35.8 mg kg$^{-1}$) was observed to be higher than that of gaseous phase PAHs (3.1 mg kg$^{-1}$, 7.2 mg kg$^{-1}$ and 5.1 mg kg$^{-1}$) from dung cakes, fuelwood and crop residue, respectively. Individually Anth, Flan, Pyr, BaA and Chry were found to be dominant in studied biomass fuels. Moreover, the average emission estimates of PAHs were determined as 2.95 ± 0.98 Gg yr$^{-1}$, 3.13 ± 1.08 Gg yr$^{-1}$ and 0.66 ± 0.26 Gg yr$^{-1}$ from dung cakes, fuelwood and crop residue, respectively.

Emission factors of PAHs were also estimated in emission from different religious and ritual burning practices including pyrolysis, flaming and smoldering in India where natural and synthetic biomaterials are used in different proportions. Five different types of religious and ritual places were selected for sampling which included Hindu Temples (HT), Muslim Holy shrines (MG), Buddhist Temples (BT), Hindu Marriage Places (MP) and Cremation Centres (Hindu Funeral Pyre) (CC). The average emission factors of total PAHs (TPAHs) was found to be 77.04±5.39, 99.09±6.02, 90.35±6.76, 22.78±1.57, and 77.15±6.16 mg kg$^{-1}$ from MP, MG, BT, HT and CC respectively. Country level emission budget of particulate bound TPAHs was found to be
0.47 Gg yr\(^{-1}\) from religious and ritual burning practices which contributed 23% of the Indian emission budget of PAHs (2.07 Gg yr\(^{-1}\)) from unknown sources [275].

Thus in Indian context, PAHs in air have been extensively studied in many urban and their adjoining areas. In various possible aspects of ambient PAHs concentrations from outdoor including particulates of different sizes, from various type of motor vehicles with different fuel used, in various urban junctions, in various period like pre CNG, post CNG etc to indoor considering variety of cooking fuel used with different possible cooking stoves, different rituals in Indian environment were considered for investigation. According to the WHO, India accounts for 80% of the 600,000 premature deaths that occur in South- East Asia annually due to indoor air pollution.

2.2.3 Soil PAHs

Soil is the main source of atmospheric dry and wet deposition. The carcinogenic potency of PAH load in traffic soil of Delhi was measured and found to be 21 times higher than as compared to the rural soil. \(\Sigma\text{BaP-equivalent concentration (BaPeq) concentration in traffic soil } (1.00943 \mu g/g) [97]\) was higher than in the roadside soil of Shanghai, China \((8.92\times10^{-1} \mu g\text{BaPeq g}^{-1}) [276]\), surface soils of Agra, India \((6.50\times10^{-1} \mu g\text{BaPeq g}^{-1}) [277]\) and in soil from Tarragona County of Spain \((1.24\times10^{-1} \mu g\text{BaPeq g}^{-1}) [278]\). Ray et al. [279] monitored PAHs in the Soil of IGI airport Delhi. The airport soil was found to be 2.58 times more contaminated with PAHs, than background soil. In the roadside soil of Jalandhar, Punjab the total average concentration of PAHs was estimated to be \(7.7\times10^{-1}\)-46.46 \(\mu g/g\) [170]. While comparing with available literature data it was revealed that Jalandhar city’s average of 16 PAHs during autumn \((16.38 \mu g/g)\) and winter \((4.04 \mu g/g)\), was quite high as compared to many other cities of the world such as Kota Bharu, Malaysia \((1.45 \mu g/g)\); Fadzil et al. [280], Australia \((3.30 \mu g/g)\); Yang et al. [96], but lower than few other cities of the world such as USA \((58.68 \mu g/g)\); Rogge et al. [134].

PAHs distribution and human health risk was also assessed in urban soils of Kurukshetra, India [281]. Environmental and human health risk assessment was carried out in terms of parameters such as BaP total potency equivalent (BaPTPE), index of additive cancer risk (IACR), life time average daily dose (LADD) and incremental
lifetime cancer risk (ILCR). The BaP total potency equivalent (BaP TPE) ranged between $8.9 \times 10^{-4}$ to 0.87 mg kg$^{-1}$ with average of 0.194 mg kg$^{-1}$. For adults and children the incremental life time cancer risk (ILCR) of PAHs was estimated as $8.1 \times 10^{-6}$ and $4.2 \times 10^{-5}$, respectively. All the estimated parameters for environmental and human health risk assessment were lower than guidelines and acceptable levels. This inferred the area is safe in terms of human exposure to soil PAHs.

Among all these studies the maximum concentration of PAHs was reported from soil of IGI airport Delhi.

2.2.4 PAHs in water

A few studies were taken up so far to estimate PAHs in water in India. Moreover, source apportionment of resultant PAHs was also scanty. Sahu et al. [252] reported PAHs in rainwater from Trombay, Mumbai. In rainwater the LMWPAHs like Phen, Flan and Pyr were dominant than the HMW compounds. Another study was carried out for PAHs in sea water of Mumbai by Pandit et al. [255]. The result of this study revealed gaseous influx in air water interface. Water of Kolleru lake wetland, east coast of India, Andhra Pradesh reported with range of total PAHs concentration $5.6 \times 10^{-2}$-$2.38 \times 10^{-1}$ µg/L and maximum concentration of BaP was $9.1 \times 10^{-2}$ µg/L [282]. Malik et al. [283] recorded the USEPA 16 PAHs in rainwater of Lucknow city. Here also it was found that the LMWPAHs like Acy (three ring PAHs) dominated over the HMW compounds which may be due to higher water solubility for LMWPAHs. The results of this study were in accordance with that reported by Sahu et al. [252] in the rainwater of Mumbai city (India) and in the rainwater of Turkey [284], however, relatively lower levels have been reported in the rainwater of Singapore [285]. Rainwater of Lucknow was the highest reported total PAHs till now.

2.2.5 River Sediment PAHs

As river and lake are the main source of water for majority of Indian population, their sediment toxicity with PAHs is now a major concern for researchers along with its ecotoxicological effects. In the bank sediment of one of the important river of India,
Yamuna, level of PAHs was measured. A comparison with earlier studies across the world reveals that PAH concentrations reported here were on the higher side [286]. Amaraneni [282] reported PAHs in the sediment of Kolleru lake wetland in east coast of India, Andhra Pradesh. The result of the study indicated that the lake need proper management as this lake is often used for prawn culture. In the Gomti river sediment, Lucknow USEPA 16 PAHs was measured. This study revealed that some sites of the river may lead to occupational risk for PAHs [287].

As mangrove has many ecological importance for the environment; PAHs in sediment cores of Sundarban mangrove wetland was also monitored. This study found that from an ecotoxicological point of view, the study sites appear to be moderately polluted [288]. Choudhory et al. [289] studied PAHs in sediment Cores from the deepest part of Nainital and Bhimtal respectively, the two Kumaun Himalayan lakes, northwest India in Uttarakhand. The concentrations in the lakes are much higher than in other remote lakes over the world. Among all these studies of PAHs on sediment, concentrations in Nainital and Bhimtal having great ecological significance was found to be highest and is of major concern.

### 2.3 Sources of PAHs in Environmental Matrices, Indian Context

Researchers had applied various methods for source apportionment of PAHs. Due to similar chemical nature certain PAHs and their ratios were used by researchers as marker for source study in the environment. Also multiple regression and principal component analysis were frequently used for source identification of PAHs.

Results of diagnostic ratio of BaP/BgP indicated a greater contribution of the traffic sources to the ambient concentrations of PAHs in two stations of Bhilai [212]. The qualitative source apportionment presented in particulate of Mumbai indicated the large amount of Pyr was likely from cooking-fuel combustion (animal manure, kerosene and liquid petroleum gas) in addition to vehicular emissions. At the Bombay IIT site, primarily vehicular emissions along with cooking fuel emissions were the likely contributors while industrial oil burning was an additional contributor at Saki Naka, accounting for the higher concentrations of Pyr and Chry/BaA [246].
With growing concern among researchers for vehicular sources of PAHs mainly in urban areas; PAHs profile in Indian cities with various types of vehicles with unique use of fuel was reported. PAHs in the exhaust from three different types gasoline driven vehicles cars, autorickshaws and scooters in Delhi was monitored. The percentage contribution of BaP to $\sum$PAHs was 1.1%, 2% and 2.6% for cars, autorickshaws and scooters respectively. The reason for such high concentration of PAHs in the present study as compared to the concentration reported elsewhere could be the age of the vehicles, driving condition, quality of the fuel, engine conditions etc [290]. A similar type of study in Delhi in two different type vehicles (buses and truck) which use diesel as fuel was performed. The PAHs concentration was found to be higher in case of truck than bus [291].

Qualitative analysis using marker compounds suggested that biomass and/or refuse burning and motor vehicle exhaust emissions were found to be primary contributors to the organic fraction of ambient PM$_{10}$ in the residential sites of southern Delhi [251]. Molecular diagnostic ratio analysis for PAHs in PM$_{10}$ suggested that diesel emission was the major source contributor in 1998 and gasoline for 2004 in Delhi [254]. Source apportionement study in total PAHs concentration in TSPM at Nunhai, Agra through correlation analysis revealed that LMWPAH was mainly due to primary emission from diesel exhaust while the HMWPAH were formed during combustion process, while good correlations between BkF, IP, Flan and Pyr indicated the contributions from gasoline and diesel combustion. Molecular diagnostic ratios of Flan/(Flan+Pyr), BaP/(BaP+Chy) and BaA/(BaA+Chy) with values 0.38, 0.8 and 0.66 respectively were indicating contributions from diesel combustion whereas IP/(IP+BgP) and IP/BgP ratios of 0.33 and 0.49 respectively were comparable to that for diesel and gasoline emissions. Moreover IP/BgP and BaP/BgP ratio indicated the dominant contribution from traffic emissions [258]. With same source identification method in another study of Agra, prevalent contribution of sources such as vehicular emission from gasoline and diesel engine were identify to contribute particulate PAHs [259]. Factor analysis of PAHs in airborne particulate (PM$_{10}$) from Agra implied that the sources were strongly linked to land use at each particular site [260]. The correlation analysis of PAHs in Agra during winter season (November 2006 to February 2007) suggested that gas utilities, cooking (frying and oil combustion), smoking and incense burning were mainly attributed to PAHs in indoor environment [260]. Source apportionment of
Gaseous/particulate bound PAHs of outdoor rural environment in Agra with correlation and factor analysis indicated cooking/diesel fumes, burning of biomass fuel (cow dung cakes/wood/coal) as potential sources of PAHs [260]. Factor analysis suggested that vehicular emissions of petrol and diesel-driven engines inclusively contributing to PAHs in PM$_{2.5}$ as probable sources in Chennai [264]. The results of diagnostic ratio and enrichment factor analyses in PAHs in PM$_{10}$ and PM$_{2.5}$ at G.G.S.I.P University campus in Delhi 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 major pollutant sources for PAHs [265]. The principal sources identified for PAHs in ambient aerosol particles at six different sites in Delhi were vehicular emission and coal combustion. Some contribution from biomass burning was also detected [266]. Principal component analysis–multiple linear regression (PCA-MLR) technique revealed mainly four sources with their respective percentage contribution of crustal dust (73%), vehicular emission (21%), coal combustion (4%) and industrial emission (2%) for PAHs in PM$_{10}$ from JNU campus in Delhi that was further validated by hierarchical cluster analysis (HCA) [173].

The use of PAHs and inorganic (metals) tracers like Fe, Mn, Cd, Cu, Ni, Pb, Zn, Cr etc being co-emitted from similar sources such as biomass burning, coal and petroleum combustion, vehicular emissions, coke and metal production etc. improve the process of source apportionment to get higher resolution results. In Indian context a few such studies were performed by Sarkar et al. [173], Amaraneni [282], Singh et al. [265], which reported their similar emission source. So, this is another very important aspect to be explored for researchers while executing PAH study.

In some of the studies source apportionment of PAHs in soil and sediment through marker compounds and statistical analysis was also adopted. In the source apportionment study of bank sediment of Yamuna river the value of Phen/Anth ratio, 0.69 ± 0.54 (<10) and BaA/Chry ratio, 3.16±2.87 (>1) in the studied samples demonstrate the classical role of pyrogenic sources. While average value of Flan/Pyr ratio, 0.92±0.62 suggested common sources i.e. combustion as well as petroleum also. In the present study average of ratios Anth/Anth+Phen, Flan/Flan+Pyr, and BaP/BaP+Chry at all the sites showed that PAH in river sediments are derived primarily from combustion sources including fossil fuels (gasoline, crude oil, and coal) and biomass
(wood and grasses) [286]. Factor analysis and isomer pair ratios suggested pyrogenic origin of PAHs in the Soil of IGI airport Delhi [279]. Principal Component Analysis (PCA) provided the fingerprints of vehicular traffic emission and coal combustion in the urban traffic sites in Delhi and IP/BgP ratio indicated that PAH load at the traffic sites is predominated by the gasoline-driven vehicles [97]. According to observed molecular indices, PAHs contamination in the river Gomti seemed to be originated both from the high temperature pyrolytic process as well as from the petrogenic source, indicating a mixed PAH input pattern [287]. To assess the PAH sources in the sediment of Nainital and Bhimtal lake, diagnostic ratios were calculated including: (i) $\sum_{LMW}$ (Naph, 2-methylnaphthalene, 1-methylnaphthalene, Acy, Acen, Flu, Phen and Anth) to $\sum_{HMWPAHs}$ (1-methylpyrene and 2-methylpyrene) and (ii) Phen to Anth. Nainital sediments reveal a dominance of LMW over HMWPAHs. In contrast, the Bhimtal sediments were found to be dominated with HMWPAHs completely. This implied that PAHs in these lakes were derived from petrogenic sources [292, 293] and are mainly of anthropogenic origin [289]. The PAH diagnostic ratios indicated that the PAHs in the sediment cores of Sundarban mangrove wetland were mainly of pyrolytic origin, mainly transported by surface runoffs [288].

Moreover, Indian soil (Delhi soil) PAHs witnessed a significant correlation with black carbon which could be used as a better predictor for PAHs presence [151]. So, this is another very important aspect of PAHs study having a lot of scope for researchers of this country.

In Indian context the preliminary studies of PAHs mainly begins with the most toxic indicator of PAHs i.e. BaP and their concentration in the ambient environment. The frontline analysis of these compounds was performed with spectrofluorometer [243,244].

In the 1990s PAHs study extended from just BaP to a group of 8PAHs and then 12PAHs compounds. Accordingly the analytical methods also upgraded with HPLC system with UVA detector and HPLC with florescence and GCMS detector [212, 245]. In the 21st century the scope of majority of studies now look into USEPA recognized 16PAHs concentrations or the no of compounds are selected according to the importance and viability of the work. For PAHs study sample preservation and method development often encounter some limitations. In most of the Indian studies on PAHs, researchers are following the classical methods of USEPA or methods developed by the
researchers of western countries. Going through all these literature, it seems there is a very urgent need for detailed and systematic study of PAHs in various environmental matrices in Indian conditions. This part of South Asia with different climatic, topography, green cover, cultural and ethnic groups thus encourages divergent scopes of monitoring of environmental exposure to PAHs.

In India, although different aspects of atmospheric PAHs were assessed by researchers, studies on atmospheric bulk deposition of PAHs are observed to be scarce. Atmospheric bulk deposition of PAHs is the comprehensive pathway for transfer of these compounds to other environmental matrices. In India, prevailing atmospheric conditions during different seasons of the year are unique. Thus, the factors governing bulk deposition of PAHs in India are quite discrete from that of other parts of the world. As we have for the first time attempted to estimate PAHs in bulk deposition and their signature in other environmental matrices, these information will act as baseline for further studies of bulk deposit PAHs in Indian context.