RASĀYAN *J. Chem.*
Vol. 9 | No. 2 |243 - 253 | April - June | 2016
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

A REVIEW ON DEPOSITION OF ATMOSPHERIC PAHs AND INTERACTION WITH OTHER ENVIRONMENTAL MATRICES AND ITS SOURCE APPORTIONMENT WITH RESPECT TO INDIAN SCENARIO

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ABSTRACT
Atmospheric bulk deposition of PAH_s 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 PAH_s in India are quite discrete from that of other parts of the world. In our literature survey, an attempt has been made to study the contribution of bulk deposition PAH_s into various other environmental compartments including soil, street dust, river water and sediment. PAH_s are a unique class of organic pollutants containing 2 or more fused aromatic rings, which are very lethal and potent carcinogens. Their occurrence has been reported from various places which indicates their ubiquitous nature of our environment. USEPA has already listed 16PAH_s as most priority ones to be analysed in various environmental matrices. The meteorological parameters played a significant role in atmospheric deposition of PAH_s with temperature dependent scavenging for $LMWPAH_s$. The exposure risk for PAH_s in all the environmental matrices was found to be the maximum during dry season.
Keywords: PAH; Environmental Matrix; Soil, Street Dust, River, Sediment; Organic Pollutant; Carcinogens; USEPA; Exposure Risk.

INTRODUCTION

The omnipresent Polycyclic Aromatic Hydrocarbon (PAH_s) compound in the environment, mainly arising from anthropogenic sources [1]. Atmospheric PAHs are derived from combustion and volatilization [2]. Aerial movement is one of the major pathways for environmental distribution and transboundary deposition of PAH_s[3]. Remote areas far from emission sources also get exposed to PAH_s as they undergo long range transport[4,6]. Eventually, PAH_s settle down in soils, street dust and enter into the aquatic environment. Soil and street dust acts as a direct sink of atmospheric PAH_s near to traffic and other combustion sources. From these environmental compartments rain water and storm water easily washed away PAH_s to nearby aquatic bodies. Due to hydrophobic nature, PAH_s in aquatic environments are preferably partitioned and accumulate into the particulate phase of sediment[6]. PAH_s thus, occur in a multicompartmental system in the environment and paved the way for multiple routes of exposure to this class of carcinogen.

PAH_s in the Atmosphere

It is fully established that the atmospheric transfer is the principal pathways for the global distribution of PAH_s[3]. Once in the atmosphere, depending on their properties such as vapour pressure, Henry's law constant and solubility, PAH_s get distributed between gas, particle and droplet phase[8]. At ambient temperature, the 2 and 3 ring PAH_s are mainly found in the vapour phase, while 4 to 6 PAH_s occur in the particle phase as recorded in the literature[9]. Oxidative and photolytic reactions and atmospheric fallouts are two major pathways for wash-out mechanism of PAH_s from the atmosphere[10]. PAHs associated with both vapour and particle phase are removed from the atmosphere by atmospheric bulk (dry+wet) deposition[8]. Deposition of PAH_s is also influenced by particle phase concentration and meteorological factors[11]. The Significant relationship of PAH_s with temperature and relative humidity was also documented[12, 13]. Moreover, it has been found that temperature variation has a more profound influence on gas phase Low molecular weight ($LMWPAH_s$) dispersion than on particulate phase High molecular weight ($HMWPAH_s$)[14].

PAH_s Deposition on Soil

In the soil surface combustion products are deposited back from the atmosphere. Soil is, therefore, considered as the medium for accumulation and integration of many pollutants[15]. Soil contamination with PAH_s is a growing problem mainly in urban areas because of increased energy consumption[16]. Such increase over time is an indicator of increased emission associated with industrialization and urbanization besides emission from motor vehicles. Emissions arising from motor vehicles are usually contributed by a mix of tailpipe emissions, wear and tear of brakes and tyres and re-suspension of street dust[17,18]. Generally, higher presence of $HMWPAH_s$ typically means contribution from combustion sources (pyrogenic) and, on the other hand, $LMWPAH_s$ are often considered to be petrogenic. Much of the combustion derived PAH_s are present in the top layer of soil and human exposure to PAH_s through soil has been reported to be greater than that of air and water[19,20].

Air to surface precipitation is the primary input of PAH_s into soil surface[21, 22]. Therefore, Soil act as major sinks of atmospheric PAH_s[23]. Further, volatilization, irreversible sorption, percolating, accretion by plants and biodegradation are the mode of dispersion of PAH_s[24]. Soil PAH_s can also be considered as a source of air and sediment contamination because of their distribution by surface runoff and dust resuspension[25]. PAH_s concentration in soil consociates well with their representative levels in air, house dust and urban street dust [26,27,28]. PAH_s soil monitoring is one of the best excellent matrix indices for pollution and environmental risk. Hydrophobic nature and chemical stability of PAH_s favour adsorption to earthy particles, thus PAH_s can sustain in the soil matrix for longer time. Thus, PAHs are persistent and poorly degraded contaminants of the soil.

PAH_s Deposition on Street Dust

Street dust is chemically most identical to the principal portion of atmospheric aerosol and exhibit a vital relationship through continuous process of re-suspension into and re-deposition from atmosphere[21]. Rapid urbanization triggering transport of increasing population and goods by a large number of motor vehicles have given rise to intensifying levels of pollution along roadways. Traffic density and rate of deposition are assumed to be the main determining factor for PAH_s concentration in street dust collected[30].

It is often considered that Street dust as the direct sink of deposited PAH_s near to sources mainly from traffic. It is very much reasonable that closer to the highway faster deposition of exhaust aerosol droplets occurs; while going away dust particles that are dispersed by wind interfered their adsorption and subsequently affect other environmental matrices (e.g. air, water, soil and plants)[31,32]. This in turn increases significant exposure risk for human population mainly for those who live by roadside[33]. Although atmospheric removal of anthropogenic and biogenic sources of PAH_s contribute to street dust load, part of street dust PAH_s may transfer back to the atmosphere through the mechanism of evaporation and wind raise[34,35].

PAH_s are easily washed out from street dust by rain to drainage and then move to nearby water bodies such as river, estuaries etc.[36] More than 95% contribution fraction of PAH_s from dry deposition was could be found on street dust and motor vehicles account for a significant aid to total PAH_s load in street dust[34]. PAH_s in urban street dust are originated from multiple sources such as weather beaten materials of road soil surfaces, vechile dissipate, grease and oils lubricating, gasoline and diesel energy, eroded tire particles and atmospherically aerosol deposited materials[37].

PAH_s Deposition on Water and Sediment

Surface water and sediment monitoring give data regarding anthropogenic happenings adjacent to a water body. Direct wet or dry deposition are the primary pathways of PAH_s entering into the aquatic environments from the atmosphere, including runoff from land, streets, asphalts, building roofs, sewer, industries, municipalities and direct water outlet[38]. In general man made sources of PAHs in water bodies can be both heatgenic and fossilogenic. Heatgenic sources of PAH_s include combustion of petrochemical, coal and biomass etc. Petrogenic PAH_s (from crude and refined petroleum products) can enter aquatic environments through accidental spraying of oil spills, solid municipal waste runoff and industrial processes. Storm water is one of the a chief distribution routes of PAH_s to the unloading water bodies irrespective of its emission sources in urban areas. Therefore, to monitor effective control and planning their source and sink has to comprehend well, so that there can be remediation[39]. In urban soils non-homogenous distributions of PAH_s are observed[40]. Upon entering aquatic systems, PAH_s preferably tend to settle, partition or adsorb onto non aqueous phase such as soil or sediment due to their hydrophobicity and high octanol/water partition coefficients[41]. After adsorption to solid surface PAH_s makes these substratum less susceptible to degradation[42]. So, the presence of PAH_s in the water system of a river can also be used as an indicator of their presence in sediment.

Much attention of a local authority has been attracted due to their mutagenic and carcinogenic effects to land and water organisms, distribution and sources of PAH_s in the aquatic environment near urban centres[43]. As per the Water Framework directive 2000/60/EC 16 PAH_s is considered as priority substances due to their toxic environmental behavior and their carcinogenic effects. High toxicity, high stability in the environment and lipophilic nature of PAH_s enable them to transport through food chains with human being as final destination[44].

The EU Directive 98/83/EC, relevant to drinking water, has set a limit of 0.10 μ g/l for the sum concentration of BbF, BkF, BgP and IP and 0.010 μg/l for BaP[45]. Thus, monitoring of these compounds in surface water can provide inputs for potential toxic effect assessment of these pollutants in addition to decision-making for management authorities[46].

Indian Scenario of PAH_s

While in many European countries studies on environmental PAHs initiated in the 1960_s, most of the studies, on the similar lines, in India started in the early 1980_s 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 PAH_s in various matrices, including soil, sediment, water and atmospheric particulate matter.

Atmospheric PAH_s

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

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

In one of the pioneering study in India, BaP levels in the air of the general community, near domestic fire pots in the kitchen and traffic junction in Ahmedabad were reported[47]. This study identified high BaP concentrations in urban conditions and opined that an association between urban-rural gradient of respiratory related cancer and durational environmental exposure of BaP 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), reported BaP concentrations in atmospheric particulate matter of urban, suburban and rural region of Bombay and made attempts among different group of populations to find a possible correlation of BaP with respiratory related cancer. Wide spatial variations of BaP levels were observed and they opined that such variation could indicate suitability for epidemiological investigations[48].

Urban PAH_s 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. The Range of average PAH_s concentration in aerosol in Indian Institute of Technology (IIT) Bombay and Regional Telecommunications Training Centre Saki Naka, Mumbai was found to be 2.1×10^{-2}-4.2×10^{-2} μg/m^3 [49]. They presented a very interesting finding on the adsorptive behavior of PAHs; predominance of non volatile PAH_s in the fine mode and semi-volatile ones in the coarse mode. Later, Kulkarni et al. reported $\sum PAH_s$ concentration range of 2.45×10^{-2}-3.88×10^{-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[50].

As concerns over PAH_s grew, groups in lesser known cities like Bhilai industrial city, started assessments with respect to health risks[51].

Researchers at NEERI conducted a very early study from 1991-2005 to see the ambient air quality status for the PAH_s 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 (243.8-1481μ g/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 PAH_s[52].

Ambient PAH_s were monitored in residential and industrial areas of Delhi in 1998 during winter, summer and monsoon and this study were reported in CPCB[53]. The concentration of PAH_s during winter, summer and monsoon was 30.3-60.9 ng/m^3, 16.0-29.3 ng/m^3 and 9.4-27.8 ng/m^3 respectively So, maximum PAHs level was observed in winter[54].

A pilot study was carried out to examine the PAH_s 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 and also inferred that local source signatures are needed to get a complete picture of organic fractions of urban aerosols[55,56].

Simultaneous rain and air sampling was performed for the 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 PAH_s the particle phase scavenging ratio values were found to be higher[57].

Suspended particulate matter samples were collected in the Jawaharlal Nehru University Campus for PAH_s 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[58].

Alternative fuel is the very way out for air quality improvement. Keeping this in mind the comparative investigated study of PAH_s 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 the use of alternative fuel could lead to 58-68% reduction of ∑PAH concentration[59].

A study has been carried out on PAH_s in ambient air of the creek area to investigate the gas influx direction in the air water interface. The study revealed the active transfer of LMW dissolved PAH_s into the atmosphere due to volatilization and deposition of HMW gas-phase PAH_s into the surface water[60].

Levels of 3PAH_s 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/m^3, BDL-1.28×10^{-1} μg/m^3 and BDL-1.01×10^{-1} μg/m^3 , 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. An Enhancement in the disintegration rate of organic compound in summer was the reported possible cause of such concentration trend[61].

PAH_s in the SPM and RSPM were studied in airborne PM in a petroleum refinery in the west coast of India in six directions. A comparison of the PAH_s concentrations showed that the average PAH_s concentrations in major Indian cities were in the range of 5.81×10^{-1}–9.6925×10^{-1} µg/m^3, which is less than the PAH_s concentration of 10.92-100.82 µg/m^3 around the refinery[62].

In Nunhai, an industrial site in Agra total PAH_s 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. During cold periods there is 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[63]. A similar study conducted on PAH_s in the same area from May 2006 to September 2006. The results indicated that PAH_s 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[64].

Measurement of 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 PAH_s concentration[65]. The PAH concentrations in industrial (9.79×10^{-2} µg/m^3), residential (3.46×10^{-2} µg/m^3) and roadside ($2.87\ \times10^{-2}$µg/m^3) areas of Agra below when compared with the Taiwan (0.1201µg/m^3)[industrial] and 7.45×10^{-2} µg/m^3 [residential] and Italy/Chile (5.48×10^{-2}/7.68×10^{-2} µg/m^3 [roadside]), respectively[66,67,68]. In the present study, the concentration of PAH_s (8×10^{-3} µg/m^3) 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[69].

In Ambathur, Kolathur, Saidapet, and Egmore is representing urban, commercial, urban-residential, and industrial regions of Chennai PAH_s in $PM_{2.5}$ were measured and found higher than (National Ambient Air Quality Standard) NAAQS annual average of 1ng/m^3 indicating an alarming pollution level in Chennai[70]. The monitoring of PAH_s in PM_{10} and $PM_{2.5}$ at G.G.S.I.P University campus in eastern part of Delhi. This study found a concentration of both PM_{10} and $PM_{2.5}$ higher than the prescribed limit of WHO and the NAAQ given by CPCB India. ∑PAH concentrations for PM_{10} and $PM_{2.5}$ were much higher in winter as compared to summer with predominance of 4-6 ring PAHs (80-95.8% of ∑PAHs)[71].

The measurement of $4PAH_s$ (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 PAH_s concentrations, in most of the cases, increase with a decrease in the size of PM, having a minimum concentration in >10.9 µm size and maximum in <0.7 µm[72].

PAH_s in ambient respirable particles PM_{10} from Jawaharlal Nehru University campus (JNU) in Delhi were recorded. Nearly 85% of the PAH_s 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 characterisations in atmospheric particulate were conducted which revealed a better result for source apportionment[73].

A passive air sampling was carried out to estimate ambient PAH_s 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 PAH_s. Seasonal variation was observed for PAH_s, it was observed that during autumn and winter there were higher concentration when 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 PAH_s. Sources of PAHs were identified to be both local and long range transport of southern Indian cities including Indian coastal regions and from Bangladesh[74].

Soil PAH$_s$

Soil is the main source of atmospheric dry and wet deposition. The carcinogenic potency of PAH load in the traffic soil of Delhi was measured and found to be 21 times higher than as compared to the rural soil. ∑BaP-equivalent concentration (BaPeq) concentration in traffic soil (1.00943 µg/g) was higher than in the roadside soil of Shanghai, China (8.92×10^{-1} µgBaPeq/g), surface soils of Agra, India (6.50×10^{-1} µgBaPeq/g) and in soils from the Tarragona County of Spain (1.24×10^{-1} µgBaPeq/g) [19,75,76,77]. Monitoring of PAHs has been carried in the Soil of IGI airport Delhi. The airport soil was found to be 2.58 times more contaminated with PAH$_s$, than background soil[78]. In the roadside soil of Jalandhar, Punjab the total average concentration of PAH$_s$ was estimated to be 7.7×10^{-1}-46.46 µg/g[70]. While comparing with available literature data it was revealed that Jalandhar city's average of 16 PAH$_s$ during autumn (16.38 µg/g) and winter (4.04 µg/g), was quite high as compared to many other cities of the world such as Kota Bharu, Malaysia (1.45 µg/g); Australia (3.30 µg/g); but lower than few other cities of the world such as USA (58.68 µg/g),[79,80,17].

PAH$_s$ distribution and human health risk were also assessed in urban soils of Kurukshetra, India. The parameters they considered were BaP total potency equivalent (BaPTPE), lifetime average daily dose (LADD), index of additive cancer risk (IACR) and incremental lifetime cancer risk (ILCR). The BaP total potency equivalent (BaP TPE) ranged between 8.9×10^{-4} to 0.87 mg/kg with an average of 0.194 mg/kg. For adults and children ILCR of PAH$_s$ was estimated as 8.1×10^{-6} and 4.2×10^{-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 PAH$_s$[81].

Among all these studies the maximum concentration of PAH$_s$ was reported from soils of IGI airport Delhi.

PAHs in water and River Sediment

A few studies were taken up so far to estimate PAH$_s$ in water in India. Moreover, source apportionment of resultant PAH$_s$ was also scanty. PAH$_s$ concentration has been reported in rainwater from Trombay, Mumbai[57]. In rainwater the LMWPAH$_s$ like Phen, Flan and Pyr were dominant than the HMW compounds. Another study was carried out for PAHs in sea water of Mumbai[60]. The result of this study revealed gaseous influx in the air water interface. Water of Kolleru Lake, wetland, east coast of India, Andhra Pradesh reported with range of total PAH$_s$ concentration 5.6×10^{-2}-2.38×10^{-1}µg/L and maximum concentration of BaP was 9.1×10^{-2} µg/L [82]. PAH$_s$ has been recorded in the rainwater of Lucknow city, Here also it was found that the LMWPAH$_s$ like Acy (three ring PAH$_s$) dominated over the HMW compounds which may be due to higher water solubility for LMWPAH$_s$[83]. The results of this study occurred in accordance with that reported by Sahuin Mumbai city (India) and in the rainfall occur in Turkey, however, relatively lower levels have been reported in the rainwater of Singapore[57,84,85]. In the bank sediment of one of the important river of India, Yamuna, level of PAH$_s$ was measured. A comparison with earlier studies across the world reveals that PAH concentrations reported here were on the higher side[86]. Amaraneni reported PAH$_s$ in the sediment of Kolleru Lake, wetland in east coast of India, Andhra Pradesh[82]. The result of the study indicated that the lake needs proper management as this lake is often used for prawn culture. In the Gomti river sediment, Lucknow USEPA 16 PAH$_s$ was measured. This study revealed that some sites on the river may lead to occupational risk for PAH$_s$[87]. As mangrove has many ecological importance for the environment; PAH$_s$ in sediment cores of Sundarban mangrove wetland was also monitored. From an ecotoxicological consideration this study found to appear moderately polluted[88.] The study of PAH$_s$ in sediment Cores from the deepest part of Nainital and Bhimtal respectively, the two Kumaun Himalayan lakes, northwest India in Uttarakhand. The concentrations PAH$_s$ in the lakes when compared with other remote lakes over the world it was found to be much higher [89].

Rainwater of Lucknow was the highest reported total PAH$_s$ till now. Among all these studies of PAH$_s$ on sediment, concentrations in Nainital and Bhimtal having great ecological significance were found to be highest and is of major concern.

Sources of PAHs in Environmental Matrices

Researchers had applied various methods for source apportionment of PAH_s. Due to similar chemical nature certain PAH_s 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 PAH_s. The results of the diagnostic ratio of BaP/BgP indicated a greater contribution of the traffic sources to the ambient concentrations of PAHs in two stations of Bhilai[51.] 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, accounting for the higher concentrations of Pyr and Chry/BaA[50]. With growing concern among researchers for vehicular sources of PAH_s mainly in urban areas; PAH_s profile in Indian cities with various types of vehicles with unique use of fuel was reported. PAH_s in the exhaust from three different type gasoline driven vehicles, cars, autorickshaws and scooters in Delhi was monitored. The percentage contribution of BaP to $\sum PAH_s$ 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 conditions, the quality of the fuel, engine conditions etc[90]. A similar type of study in Delhi in two different type vehicles (buses and truck) which use diesel as fuel was performed. The PAH_s concentration was found to be higher in case of truck than bus[91].

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[56]. Molecular diagnostic ratio analysis for PAH_s in PM_{10} suggested that diesel emission was the major source contributor in 1998 and gasoline since 2004 in Delhi[59.] Source apportionment study in total PAH_s 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 the 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[63].

With the same source identification method in another study of Agra, the prevalent contribution of sources such as vehicular emission from gasoline and diesel engine was identified to contribute particulate PAH_s[64]. 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. The correlation analysis of PAH_s in Agra during winter season (November 2006 to February 2007) suggested that gas utilities, cooking emission of frying and oil combustion due to cooking, smoking and incense burning were mainly attributed to PAHs in indoor environments. Source apportionment of Gaseous/particulate bound PAH_s 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 PAH_s[65]. Factor analysis suggested that vehicular emissions of petrol and diesel-driven engines inclusively contributing to PAH_s in $PM_{2.5}$ as probable sources in Chennai[70]. The results of diagnostic ratio and enrichment factor analyses in PAH_s 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 incineration of waste, industrial combustion emission as well as natural sources associated with the transport of street dust were the major pollutant sources for PAH_s[71]. The principal sources identified for PAH_s in ambient aerosol particles detected at six different sites in Delhi were vehicular emission and coal combustion and to some extent to biomass burning as well[72]. Principal component analysis–multiple linear regression (PCA- MLR) technique revealed mainly four sources with their respective percentage contribution of crustal dust (73%), vehicular discharge (21%), coal combustion emission (4%) and industrial release (2%) for PAH_s in PM_{10} from JNU campus in Delhi that was further validated by hierarchical cluster analysis (HCA)[73].

The use of PAH_s 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 which reported their similar emission source[73,82,71] so, this is another very important aspect to be explored for researchers while executing PAH study.

In some of the studies source apportionment of PAH_s 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 the 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 bank discharge due to the combustion sources, including fossil fuels (gasoline, crude oil, and coal) and biomass (wood and grasses)[86]. Factor analysis and isomer pair ratios suggested pyrogenic origin of PAH_s in the Soil of IGI airport Delhi[78]. PCA detection is used as the fingerprints of vehicular traffic emission and coal combustion in the urban traffic sites in Delhi and IP/BgP ratio indicated that the PAH load at the traffic sites is predominated by the gasoline-driven vehicles[19]. According to observed molecular indices, PAH_s contamination in the river Gomti seemed to be originated both from the high temperature heatolytic process as well as from the petrogenic source, indicating a mixed PAH input pattern[87]. To assess the PAH sources in the sediment of Nainital and Bhimtal lake, diagnostic ratios was calculated including: (i) ∑LMW (Naph, 2-methylnaphthalene, 1-methylnaphthalene, Acy, Acen, Flu, Phen and Anth) to ∑HMWPAHs (1-methylp yrene and 2-methylpyrene) and (ii) Phen to Anth. Nainital sediments reveal a dominance of LMW over $HMWPAH_s$. In contrast, the Bhimtal sediments were found to be dominated with $HMWPAH_s$ completely[92,93]. This implied that PAH_s in these lakes were derived from petrogenic sources and are mainly of anthropogenic origin[89]. The PAH diagnostic ratios indicated that the PAH_s in the sediment cores of Sundarban mangrove wetland were mainly of pyrolytic origin, mainly transported by surface runoffs[88].

Moreover, Indian soil (Delhi soil) PAH_s witnessed a significant correlation with black carbon, which could be used as a better predictor for PAH_s presence[94]. So, this is another very important aspect of PAH_s study having a lot of scope for researchers of this country. In Indian context the preliminary studies of PAH_s mainly begin with the most toxic indicator of PAH_s i.e. BaP and their concentration in the ambient environment. The frontline analysis of these compounds was performed with spectrofluorometer[47,48].

In the 1990s PAH_s study extended from just BaP to a group of $8PAH_s$ and then $12PAH_s$ compounds. Accordingly the analytical methods also upgraded with the HPLC system with Ultra violet lamp and florescence and GCMS detector[51,49]. In the 21st century the scope of the majority of studies now looks into USEPA recognized $16PAH_s$ concentrations or the no of compounds are selected according to the importance and viability of the work. For PAH_s study sample preservation and method development often encounter some limitations. In most of the Indian studies on PAH_s, researchers are following the classical methods of the USEPA or methods developed by the researchers of western countries.

CONCLUSION

Going through all these literature, it seems there is a very urgent need for detailed and systematic study of PAH_s in various environmental in Indian conditions. This part of South Asia with different climatic, topographic, green cover, cultural and ethnic groups, thus encourage divergent scopes of monitoring of environmental exposure to PAH_s. In India, although different aspects of atmospheric PAH_s were assessed by researchers, studies on atmospheric bulk deposition of PAH_s are observed to be scarce. Atmospheric bulk deposition of PAH_s 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 PAH_s in India are quite discrete from that of other parts of the world. In our literature survey, an attempt has been made to study the contribution of bulk deposition PAH_s into various other environmental compartments including soil, street dust, river water and sediment. Among all these studies the maximum concentration of PAH_s was reported from soils of IGI airport Delhi. Rainwater of Lucknow was the highest reported total PAH_s till now. Among all these studies of PAH_s on sediment, concentrations in Nainital and Bhimtal having great ecological significance were found to be highest and is of major concern.

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[RJC-1398/2016]