International Journal of Geology, Earth & Environmental Sciences ISSN: 2277-2081
An Open Access, Online International Journal Available at http://www.cibtech.org/jgee.htm
2021 Vol. 11, pp. 70-83/Kumar et al.
Research Article

CHARACTERIZATION OF POSSIBLE SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS, USING VARIOUS DIAGNOSTIC INDICES IN SOILS FROM DEVELOPING CITY IN INDIA

Bhupander Kumar*, Virendra K. Verma, Premanjali Rai, and Sanjay Kumar
Central Pollution Control Board, East Arjun Nagar, Delhi -110032, India
**Author for Correspondence*

ABSTRACT
Polycyclic aromatic hydrocarbons (PAHs) are known to be ubiquitous in the environment. Soils are considered as source and sink for many PAHs, and play important role in their distribution. Urbanization has significant impact on all the environmental compartments, resulting in environmental quality deterioration by a variety of pollutants. No study was carried out for identification of possible source of PAHs in any matrix for this region. Hence, total 48 soil samples were collected from a developing city in India, and analysed for priority sixteen PAHs. Sample were extracted with ultrasonication technique and analyzed by HPLC equipped with diode array detector. The observed pattern shows that PAHs with 3-4 aromatic rings were dominant. The concentration of 3-ring and 4-ring PAHs ranged between 18 – 951 μg kg^{-1} and 7-824 μg kg^{-1}, and their contribution accounted for 42.26% and 32.12% to ∑16PAHs. The observed concentrations were much lower than reported PAHs in soils from various locations, and more or less comparable with the various cities in India. Possible sources of PAHs were identified through various diagnostic tools including homolog profiles, diagnostic molecular ratios, Pearson's correlation and principal component analysis. Study concluded with mixed pyrogenic sources from vehicle emissions, diesel, fossil fuel combustion and biomass combustion were the significant contributor of PAHs.

Keywords: *Priority Polycyclic aromatic hydrocarbons* (*PAHs*)*, Source Apportionment, Diagnostic tools, Soil*

INTRODUCTION
Polycyclic aromatic hydrocarbons (PAHs), the contaminants of concern are released to the environment mainly from petrogenic sources (petroleum products) and pyrogenic sources. Petrogenic sources in urban areas includes petroleum products from accidental spillage and automobile workshops. While pyrogenic sources include mainly anthropogenic activities of incomplete combustion of coal, petroleum products, woods, gases, biomass and wastes (municipal and industrial) (ATSDR, 1995). PAHs once released into the atmosphere are partitioned into particle bound phase and gaseous phase. PAHs exposures to humans increases their concentrations and accumulation in the tracheobronchial epithelium. and circulatory system through lungs. PAHs exert genotoxic effects through formation of DNA-PAH adducts (e.g., which may lead to mutations) and cause carcinogenesis (Bosetti *et al*., 2007; Schroeder, 2011; Perera *et al*., 2011; Herbstman *et al*., 2012; Gurbani *et al*., 2013). Thus, sixteen PAHs were classified as probable / possible carcinogens to humans (IARC, 2006), and listed by US Environmental Protection Agency and European Union as priority pollutants (USEPA, 2015; EC, 2001).
PAHs are known to be ubiquitous in the various environmental compartments (Wang *et al*.**,** 2009). Due to their hydrophobic nature and affinity for particulate matter (Aleksandra *et al*., 2019**)**, PAHs concentration in soil is comparatively higher than other environmental media. Soils play an important role in their distribution through volatilization, degradation and leaching (Wilcke, 2007; Li *et al*., 2018). Rapid growth of population and industrialization in urban areas have direct or indirect impact on all the environmental compartments, resulting in environmental quality deterioration by a variety of pollutants. PAHs emissions

have been well correlated with energy consumption in urban areas (Hafner *et al*., 2005). The major sources of PAH concentrations in urban soils are various anthropogenic activities including incomplete combustion of fossil fuels, various thermal processes (power plants, incinerators, vehicle engines, and cooking). Other source of PAHs in urban soils includes atmospheric depositions, sludge and compost, runoff/refuse water from asphalt roads, agriculture and automobile workshops (Williams *et al*., 2013). In recent years, PAHs has been reported in various soils from various locations in developing India (Gupta and Kumar, 2020; Ghosh and Maiti, 2020; Suman *et al*., 2016; Devi *et al*., 2016; Kumar *et al*., 2016, 2015a, Khillare *et al*., 2014; Singh *et al*., 2012). However, available literature on PAHs in environmental matrices including soils from central India is scanty (Kumar *et al*., 2015b). Few reports for this region are available on health impact of air pollutants (Dandotiya *et al*., 2019; Sharma *et al*., 2016, 2017).
Recently, Gwalior city in central India has been listed among the most polluted city in India in terms of particulate matter by World Health Organization (WHO, 2018). However, considering traffic and open waste burning as major sources of air pollution, Sharma *et al*., (2016) reported moderately polluted air quality of the city. Further, industrial activities in the vicinity are also the cause to the degradation of air quality in the city (Sharma *et al*., 2017). No study was carried out for identification of possible source of PAHs in any matrix for this region. Therefore, in this study, various diagnostic tools were used for identification of possible sources of priority PAHs in urban soils from developing city in India.

MATERIALS AND METHODS

Study Area

The sampling locations were in Gwalior city. The Gwalior city is located between Malwa plateau in the southwest and Gangetic plain in the northeast with its geographical location of $25^0$45 25.47N to $26^0$15 51.88N and $77^0$39 36.77E to $78^0$22 43.08 E. Gwalior is a major and historical city in the state of Madhya Pradesh of central India with total district area of ~4560 km^2, total population of ~2.03 million and with an urban population of ~1.27 million (2011 census). The area has a sub-tropical climate with hot summers from late March to early July. Temperatures peak in May and June with daily average of 33–35 °C. Winter starts in late October, and daily average temperature ranged between 14–16 °C, while, January is the coldest month with average lows of 5-6 °C. Gwalior receives 900 mm of rain on average per year during the humid monsoon season from June to October. Gwalior is surrounded by designated industrial areas including Sitholi, Banmore, and Malanpur with dairy, chemical, food processing, and textiles as major industrial activities. Transportation is road based with the ~13,193 numbers of registered vehicles in the city (DPES, 2016).

Solvents, Chemicals and Standards

All solvents and chemicals procured from Fisher Scientific (India) were HPLC grade and analytical grade, respectively. Activated Silica gel (100–200 mesh) used for extract clean-up was procured from Sigma-Aldrich (USA). Standard solutions of individual sixteen PAHs namely; naphthalene (Npt), acenaphthylene (ANy), acenaphthene (ANe), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(a) anthracene (BaA), chrysene (Chr), benzo(b)-fluoranthene (BbF), benzo(k)uoranthene (BkF), Benzo(a)pyrene (BaP), benzo(ghi)perylene (BghiP), dibenzo(a,h)anthracene (DBA) and indeno(1,2,3-cd)pyrene (IndP) and a mixed standard solution of 16 PAHs purchased from Supelco (Sigma-Aldrich, USA). Working standard solutions with suitable concentrations were prepared after serial dilutions of stock solutions and used for instrument calibration and quality control analysis.

Sampling and Extraction

A total number of 32 sub-surface (~10 cm depth) soil samples (~500 g each) in duplicates collected from sixteen residential locations in Gwalior, India. After manual removal of unwanted materials, aliquot of homogeneous representative samples of each location transferred to clean wide mouth amber glass containers and transported with ice to the laboratory. Air dried samples (1.0 mm sieved) extracted three times with mixture of acetone-hexane (1:1 v/v) in ultrasonic water bath (USEPA Method 3550C). Sample extracted passed through anhydrous sodium sulphate on Whatman No 41 filter paper and concentrated using a rotary evaporator (Eyela, Tokyo, Japan). Silica gel (100–200 mesh) column chromatography with methylene chloride/pentane (2:3) (v/v) as eluent was performed for clean-up of extracts (USEPA Method 3630C). Cleaned extracts containing PAHs was concentrated and solvent exchanged to acetonitrile for analysis by HPLC.

Analysis and Quality Control

Agilent HPLC equipped with diode array detector (DAD, λ=254 nm), quaternary pump and degasser was used for analysis of sixteen PAHs. Separation and quantification of PAH compounds was carried out on LC-PAH Supelcosil^{TM} (25cm x 4.6 mm, 5 µm film) analytical column and Eclipse XDB-C8 (4.6 x 12.5 mm, 5 µm) as guard column. Gradient flow of acetonitrile (65%) and HPLC water (35%) was used as mobile phase with linear flow (@1.0 ml/min) to 100% acetonitrile in 30 min (Kumar *et al*., 2014b).

Analytical quality control analysis included procedural blanks, random duplicate analysis, five-level calibration curves and calibration verification. Response in procedure blank was <detection limit. Variation in random duplicate analysis was <10%. Prior to every batch of analysis, five-point level calibration (r^2, 0.999) was performed and calibration verification was <10%. Measurements were taken in duplicate and the average value was used in calculations. The recovery study was 82%-109% for 16 PAHs and 94% for 1-fluoronaphthalene (surrogate standard). The detection limits for PAH compounds ranged between 0.09-0.21 (±0.03) µg kg^{-1} at signal to noise ratio of >3:1

Table 1: Concentration of ∑PAHs in soils.

PAHs	Concentrations (µg kg^{-1})				% of ΣPAHs
	Range	Mean	Median	SE*	
2-ring	16 - 93	35	23	4	6.9
3-ring	18 - 951	214	76	49	42.3
4-ring	7 - 824	162	86	37	32.1
5-ring	17 - 135	49	37	7	9.8
6-ring	9 - 97	45	43	5	8.9
LMW	18 - 998	233	91	73	48.9
HMW	58 - 898	248	150	54	51.1
∑16PAHs	76 - 1391	481	384	68	100

*SE=SD/√n

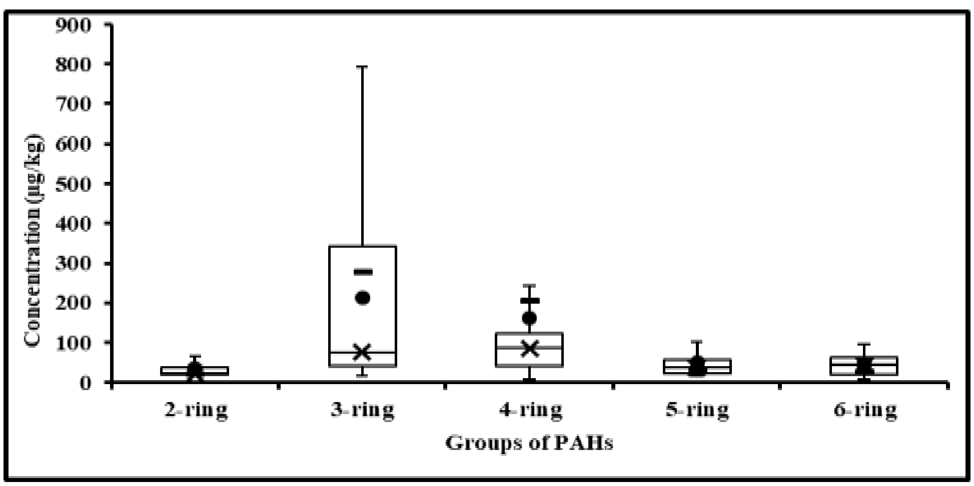

Figure 1: Concentration plot of PAHs in soil

RESULTS AND DISCUSSIONS

Concentration of PAHs with Different Aromatic Rings

Based on the presence of aromatic rings, priority sixteen PAHs classified as 2-aromatic rings (Npt), 3-aromatic rings (ANy, ANe, Fle, Phe and Ant), 4- aromatic rings (Flt, Pyr, BaA and Chr), 5- aromatic rings (BbF, BkF and BaP) and 6- aromatic rings (BghiP, DBA, and IndP). The observed order of concentration for 2- to 6 ring PAHs was 3-ring > 4-ring > 5-ring > 6-ring > 2-ring PAHs. The contribution of 2- to 6 ring PAHs to ∑16PAHs was 7%, 42%, 32%, 10% and 9%, respectively. The concentration of PAHs with 2- to 6 ring (2-ring, 3-ring, 4-ring, 5-ring and 6-ring PAHs) is presented in **Table 1 & Figure 1**. The results showed that the 3-ring PAHs (42%) and 4- ring PAHs (32%) are the most abundant groups in the studied soils, and their dominance indicated mixed pyrogenic origin of sources (Khalili *et al*., 1995; Wilcke, 2007). Among 3-ring PAHs, acenaphthene and fluorene were the dominant PAHs with their mean concentration of 429±81 µg kg^{-1} and 42±5 µg kg^{-1}, and accounted for 33% and 5%, respectively to ∑PAHs. While, chrysene (72±29 µg kg^{-1}), fluoranthene (34±11 µg kg^{-1}), and pyrene (36±16 µg kg^{-1}) were the dominants 4-ring PAHs, and their contribution was accounted for 15%, 7%, and 7%, respectively to ∑PAHs (**Figure 2**). Similar results have been reported for soil from Nigeria (Bassey *et al*. 2019), Chile (Deelaman *et al*., 2020), Jordan (Dabaibeh, 2020).

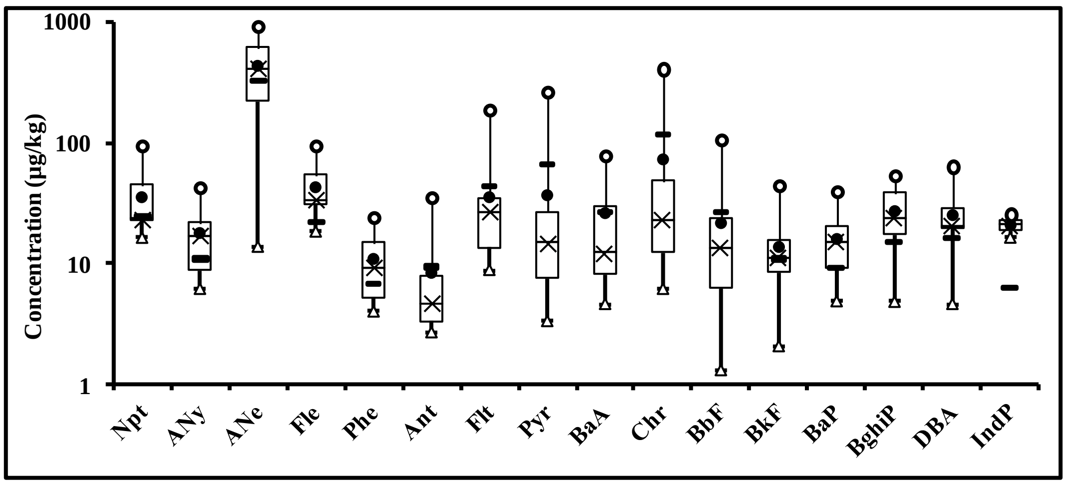

Figure 2: Distribution pattern of individual PAHs

Comparison with Other Studies

The measured concentrations of PAHs in present study were compared with similar studies on PAHs in soil from other locations in world including India. The observed concentrations of PAHs were comparable with the various locations in India, such as North-Eastern region (458 µg kg^{-1}, Devi *et al*., 2016), NCR (445 µg kg^{-1}, Kumar *et al*., 2016) and Ghaziabad (574 µg kg^{-1}, Kumar *et al*., 2015a). But, elevated levels of PAHs have been reported for soils from Delhi (3,600 µg kg^{-1}, Kumar *et al*. 2014b; 1714 µg kg^{-1}, Gupta & Kumar, 2020), Jharkhand (10,954 µg kg^{-1}, Ghosh and Maiti ,2020), and Dhanbad (3,488 µg kg^{-1}, Suman *et al*., 2016). However, low concentration of PAHs was reported in soils from Chhattisgarh, India (385 µg kg^{-1}, Kumar *et al*. 2014a). However, observed concentrations of PAHs were much lower than various locations in other countries including Orlando, USA (3,227 µg kg^{-1}, Liu *et al*., 2019), Shandong, China (3,016 µg $kg^{-1,}$ Wu *et al*., 2018), Cape Town, South Africa (4,080 µg kg^{-1}, Raissa *et al*., 2017), Kathmandu, Nepal (1,172 µg kg^{-1}, Pokhrel *et al*., 2018), Ulsan, South Korea (810 µg kg^{-1}, Kim *et al*., 2019), Rawalpindi, Pakistan (3,672 µg kg^{-1}, Saba *et al*., 2012), Gwangju, Addis Ababa, Ethiopia (800 µg kg^{-1}, Prasse *et al*., 2012) and Beijing, China (736 µg kg^{-1}, Cao *et al*., 2019). Lower concentrations than our study were reported from Gwangju, South Korea (51 µg kg^{-1}, Islam *et al*., 2018) and Tijuana, Mexico (308 µg kg^{-1}, Enrique *et al*., 2016).

Table 2: Diagnostic molecular ratios of PAHs concentration for possible sources identification

Diagnostic ratios with their reported values for possible sources				This study*
PAH ratio	**Value**	**Possible sources**	**Reference**	
LMW/HMW	<1	Pyrogenic sources	Wilcke, 2007	0.73
	>1	Petrogenic sources	Wilcke, 2007	(0.11 – 2.54)
Fle/(Fle+Pyr)	<0.5	Petrol emissions	Khaiwal *et al*., 2008	0.73
	>0.5	Diesel emissions	Khaiwal *et al*., 2008	(0.26 – 1.0)
Ant/(Ant+Phe)	<0.1	Petrogenic sources	Yunker *et al*., 2002	0.43
	>0.1	Petroleum, biomass comb.	Yunker *et al*., 2002	(0.20 – 1.00)
Flt/(Flt+Pyr)	<0.4	Petrogenic sources	Yunker *et al*., 2002	
	0.4-0.5	Fossil fuel combustion	Yunker *et al*., 2002	
	>0.5	Biomass, coal comb.	Yunker *et al*., 2002	0.59
	0.3 – 0.7	Diesel engine	Kavouras *et al*., 2001	(0.36 – 0.78)
	<1.0	Gasoline, diesel engine	Lee *et al*., 1995	
	1.0 – 1.4	Coal combustion	Lee *et al*., 1995	
BaA/(BaA+Chr)	<0.2	Petrogenic sources	Yunker *et al*., 2002	
	0.2-0.35	Petroleum comb.	Yunker *et al*., 2002	
	>0.35	Biomass, coal comb.	Yunker *et al*., 2002	0.42
	0.53	Vehicle emission	Dickhut *et al*., 2000	(0.12 – 0.85)
	0.73	Diesel engine	Rogge *et al*., 1993	
	0.79	Wood burning	Dickhut *et al*., 2000	
BbF/BkF	0.92	Wood comb.	Dickhut *et al*., 2000	
	1.07	Diesel engine	Lee *et al*., 1995	1.46
	1.30	Vehicular emission	Dickhut *et al*., 2000	(0.46 – 3.73)
	3.7	Coal combustion	Dickhut *et al*., 2000	
BaP/BghiP	<0.6	Non-traffic sources	Wang *et al*., 2007	
	>0.6	Traffic sources	Katsoyiannis *et al*., 2007	0.73
	0.3 -0.78	Vehicular emissions	Simcik *et al*., 1999	(0.12 – 1.44)
	0.9-6.6	Coal comb.	Simcik *et al*., 1999	
BaP/(BaP+Chr)	0.07-0.24	Coal comb.	Chen *et al*., 2005	0.41
	0.49	Gasoline	Khalili *et al*., 1995	(0.04 – 0.78)
	0.73	Diesel engine	Khalili *et al*., 1995	
IndP/(IndP+BghiP)	<0.2	Petrogenic	Yunker *et al*., 2002	0.42
	0.2-0.5	Petroleum comb.	Yunker *et al*., 2002	(0.37 – 0.47)
	>0.5	Biomass, coal comb.	Yunker *et al*., 2002	

*range in parenthesis

Source Apportionment

Priority PAHs can be classified according to their molecular weights i.e. low molecular weight "LMW" PAHs with <4 aromatic rings (molecular weight, 128 – 178) and high molecular weight "HMW" PAHs with ≥4 aromatic rings (molecular weight, 202 – 278). PAHs with different molecular weight in the environment have been associated with different sources. Such as dominance of HMW-PAHs in the environment are usually released from pyrogenic sources including coal combustion and vehicular emissions. While, dominance of LMW-PAHs in the environment has been associated with petrogenic sources and combustion of woods, grass and industrial oil (Wilcke, 2007). The observed mean concentration of LMW-PAHs during present study was comparatively lower 233 (±73) µg kg^{-1}, than HMW-PAHs 248 (±54) µg kg^{-1}. High concentrations of HMW-PAHs at this study area suggest local pyrogenic inputs, presumably vehicles emission, while the presence of LMW-PAHs indicates impacts of long-range transport and low-temperature combustion processes such as biomass combustions (Khalili *et al*., 1995). The observed composition profiles of PAHs suggested mixed sources in nature. Further, marginally higher levels of HMW-PAHs, and consequently low ratio of LMW-PAHs to HMW-PAHs (0.73), indicated pyrogenic origin of PAHs (Wilcke, 2007) (**Figure 2**). Dominance of HMW-PAHs in urban environments has been reported due to industrial and vehicular emissions, which have a tendency to adsorbed on the particles and rapid deposition (Singh *et al*., 2012; ATSDR, 1995). Sharma *et al*., (2017) reported vehicular emissions and waste burning as the major sources of air pollutants in the study area. While, majority of air particles in India have been reported to be contributed by vehicular emissions, construction activities, diesel generators, power plants, industries and biomass combustions (Cusworth *et al*., 2018; Sharma *et al*., 2017; Singh *et al*., 2012).

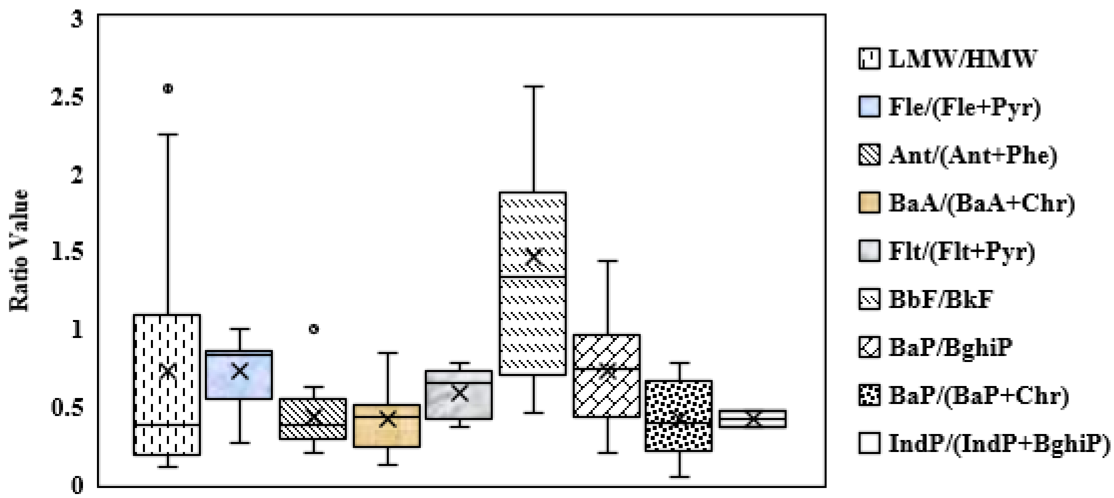

Figure 3: Diagnostic molecular ratios of PAHs concentration

Molecular Diagnostic Ratios

Characteristic ratios between selected PAHs have been used as diagnostic tools to identify the possible sources of PAHs (Kavouras *et al*., 2001). The calculated ratios between selected PAHs for this study are presented in **Table 2 & Figure 3**. Khaiwal *et al*., (2008) suggested < 0.5 and >0.5 ratio value of Fle/(Fle+Pyr) for PAHs sources from petrol emission and diesel emissions, respectively. Thus obtained ratio between Fle/(Fle+Pyr) for this study (0.73) indicated diesel emissions. Ratio value of Ant/(Ant+Phe) for present study (0.43) was > 0.1 (Yunker *et al*., 2002), suggested combustions of petroleum and biomass. Yunker *et al*., (2002) reported 0.4 – 0.5 and >0.5 ratio of Flt/(Flt+Pyr) for biomass combustion and fossil fuel combustion, 0.3 – 0.7 ratio value for diesel engine (Kavouras *et al*., 2001), <1.0 value for gasoline and diesel engine, and 1.0 – 1.4 value for Coal combustion (Lee *et al*., 1995). The observed ratio of Flt/(Flt+Pyr) (ranged, 0.36 – 0.78, mean, 0.59) for this study suggested biomass combustion and fossil fuel combustion including diesel engines as major sources of PAHs. BaA/(BaA+Chr) ratio of <0.2, 0.2 – 0.35 and >0.35 suggested for petrogenic sources, petroleum combustion and biomass & coal combustions (Yunker *et al*., 2002), 0.53 value for vehicular emissions (Dickhut *et al*., 2000), 0.73 value for diesel engine (Rogge *et al*., 1993), and 0.79 value for wood, grass, leaves burning (Dickhut *et al*., 2000). The calculated value of BaA/(BaA+Chr) ratio for present study (range, 0.12 – 0.85, average, 0.42) indicated petrogenic and mixed pyrogenic sources of fossil fuel combustions, biomass burning and emissions from diesel and petrol vehicles. Further, it is reported that >0.40 ratio of BaA/(BaA+Chr), indicates recent emissions and relatively low photochemical degradation, while, <0.40 ratio value indicates the aged sources of PAHs (Kaur *et al*., 2013). The obtained ratio of BaA/(BaA+Chr) in this present study indicating deposition of recent emissions of PAHs as well as transportation of fresh and older air masses to the study area. Lee *et al*., (1995) reported BbF/BkF ratio value (1.07) for diesel engine emissions, 1.30 for vehicular emission and 3.7 value for vehicular and coal combustion (Dickhut *et al*., 2000). The ratios of BbF/BkF obtained in this study (range, 0.46–3.73, mean, 1.46), indicated diesel vehicle emissions and coal combustions as PAHs sources. Non-traffic and traffic sources of PAHs are characterized by BaP/BghiP ratio value of <0.6 and >0.6, respectively (Wang *et al*., 2007; Katsoyiannis *et al*., 2007). However, BaP/BghiP value of 0.3–0.78 and 0.9–6.6 has been reported for vehicular emissions and coal combustions, respectively (Simcik *et al*., 1999). The estimated BaP/BghiP ratio value for studied soils (range, 0.12–1.44, average, 0.73) suggested PAHs sources from coal combustion and vehicular emission. Chen *et al*., (2005) and Khalili *et al*., (1995) suggested BaP/(BaP+Chr) value ratio for coal combustion (0.07–0.24), gasoline (0.49) and diesel engine (0.73) sources of PAHs. IndP/(IndP+BghiP) ratio value of <0.2, 0.2–0.5 and >0.5 indicates petrogenic, petroleum combustion and fossil fuel combustions as PAHs sources (Chen *et al*., 2005; Khalili *et al*., 1995). The ratio values of BaP/(BaP+Chr) and IndP/(IndP+BghiP) for this study ranged between 0.04– 0.78 and 0.37– 0.47, with the mean value of 0.41 and 0.42, respectively indicated mixed pyrogenic sources of PAHs including gasoline, diesel engine and fossil fuel combustions in study area. These results indicated that mixed pyrogenic sources of vehicles, diesel engines, gasoline, fossil fuel combustion and biomass combustion were the major sources of PAHs to the study area (Table 2). Similar sources of air pollution in the region has been reported by Sharma *et al*., (2017). However, accidental spillage and automobile workshops may be cause of petrogenic sources. Our findings on identification of possible sources of PAHs through molecular ratios are in consistent with the results of other studies for India (Kumar *et al*., 2016, 2015a, b, 2014a, b; Singh *et al*., 2012).

Pearson's moment Correlations

Correlation analysis was carried out to determine relationships between individual PAH that two or more PAHs may be correlated due to common source of PAHs origin (**Table 3**). Correlation analysis shows that there was significant correlation (*two tailed*, $p<0.01$, $p<0.001$) between the 2- to 6 ring PAHs. Results shows a significant strong correlation between 3-ring and 4-ring PAHs such as ANe, Ant, Flt, Pyr, BaA and Chr can be associated to low temperature biomass combustions sources. An another strong correlation among 3-ring PAHs to 5-ring PAHs and 6-ring such as ANe, Fle, Phe and Ant to BbF, BkF, BaP, BghiP and DBA indicated biomass, vehicular, industrial and fossil fuel combustions emissions sources. Strong correlation among 4-ring PAHs to 5-ring PAHs and 6-ring including Flt, Pyr, Chr and BaA to BaP, BghiP and DBA suggested high temperature combustion process including vehicles, industries and coal combustions sources (Khalili *et al*., 1995; Wilcke ,2007). Another correlation between 5-ring PAHs and 6-ring PAHs such as BbF, BkF, BaP, BghiP and DBA has also suggested high temperature combustion process including stationary source emissions (Kaur *et al*., 2013). The presence of designated industrial areas including Sitholi, Banmore, and Malanpur, and coal combustion emissions in the vicinity of the study area can be attributed to stationary sources. These results demonstrated the mixed pyrogenic sources of PAHs in Gwalior soils. Study concluded that mixed pyrogenic sources such as biomass and coal combustion and vehicular emissions may be the most significant sources of PAHs in the soils from Gwalior. It has been reported that combustion processes are the major sources of organic matter and elemental carbon in the Indian environment (Khanna *et al*., 2018).

Principal Component (PC) analysis

Further, for identification of possible sources of PAHs in soil from central India, principal component analysis (PCA) was performed. PCA is a multivariate statistical analysis to transform the original data set into a smaller one that account for most of the variance of the original data (Singh *et al*., 2012; Khillare *et al*., 2014). Four Principal Components (PC) explaining 82.29% of the total variance are presented in **Table 4**. Using PCA, four different factors were identified using eigenvalue >1, explaining 82.29% of the total variance, of which 39.15%, 26.06%, 10.12% and 6.96% is explained by PC1, PC2, PC3 and PC4, respectively. As loading values were low, could be due to the nature of the entire data set, a factor loading at >0.20 was selected as the lowest level of significance for identified components. However, loadings of marked PAHs were significantly higher compared with other PAHs in the same component. PC1 with

Table 3: Pearson's moment Correlation Coefficient

Rings	PAHs	2-ring	3-ring					4-ring				5-ring			6-ring		
		Npt	ANy	ANe	Fle	Phe	Ant	Flt	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	DBA	IndP
2-ring	Npt	1.00	-0.17	0.56[a,b]	-0.93	0.16	-0.35	-0.27	-0.20	-0.57	-0.41	-0.22	0.39	-0.15	-0.49	-0.06	-1.00
3-ring	ANy		1.00	-0.35	-0.31	-0.36	-0.11	-0.43	-0.41	-0.58	-0.46	-0.17	0.20	-0.15	0.25	0.24	-1.00
	ANe			1.00	-1.00	-0.08	-0.54	0.95[a,b]	0.91[a,b]	0.28	0.32	0.06	0.80[a,b]	-0.20	-0.38	0.80[a,b]	-1.00
	Fle				1.00	-0.03	0.92[a,b]	0.83[a,b]	0.79[a,b]	0.76[a,b]	0.57[a,b]	0.16	-0.14	-0.26	0.49[a]	0.49[a]	-1.00
	Phe					1.00	0.42	-0.02	-0.02	0.65[a,b]	-0.13	0.49[a]	-0.15	0.50[a]	0.23	0.01	-1.00
	Ant						1.00	0.19	0.20	0.36	0.22	-0.08	-0.34	-0.04	-0.06	0.86[a,b]	-1.00
4-ring	Flt							1.00	0.98[a,b]	0.58[a,b]	0.54[a]	-0.07	0.06	-0.17	0.18	0.93[a,b]	-1.00
	Pyr								1.00	0.58[a,b]	0.46[a]	-0.04	0.19	-0.08	0.10	0.89[a,b]	-1.00
	BaA									1.00	0.27	0.41	-0.05	0.44[a]	0.35	0.31	1.00
	Chr										1.00	0.08	-0.11	-0.26	0.44[a]	0.57[a,b]	1.00
5-ring	BbF											1.00	0.27	0.54[a]	0.61[a,b]	0.29	1.00
	BkF												1.00	0.30	0.17	0.69[a,b]	-1.00
	BaP													1.00	0.37	-0.06	1.00
6-ring	BghiP														1.00	0.17	1.00
	DBA															1.00	-1.00
	IndP																1.00

[a] and [b] denotes significant correlations at $p<0.01$ and $p<0.001$, respectively.

39.15% of the variance had high loadings for ANe, Fle, Flt, Pyr, BaA, Chr & DBA PAHs. The dominant presence of three- and four-ring PAHs in PC1 is indicative of long range transport (Khillare *et al*., 2014). The presence of Fle, Flt, Pyr, BaA, Chr & DBA are markers for coal combustion (Khalili *et al*., 1995; Wilcke, 2007; Ravindra *et al*., 2008).

PC2, the second component accounted for 26.06% of the variance, and loading with Fle, Phe, BaA, BbF, BaP, BghiP & IndP PAHs. Dominance of BbF, BaP, BghiP, & IndP are high temperature combustions sources from heavy duty diesel powered vehicles, industries and stationary emissions (Khalili *et al*., 1995; Simcik *et al*., 1999; Dickhut *et al*., 2000; Chen *et al*., 2005). Phe, Pyr, BaA and Chr are typical indicators of wood combustion (Khalili *et al*., 1995). Therefore. PC2 has been attributed to diesel, and wood combustion. The third component, PC3 with 10.12% of the variance was loaded by BbF, BkF & BghiP PAHs are indicatives of diesel vehicles (Khalili *et al*., 1995; Ravindra *et al*., 2008; Khillare *et al*., 2014). PC4 with 6.96% of the variance and with higher loadings of the ANy & BghiP PAHs are indicative of biomass, and wood combustion sources (Khalili *et al*., 1995; Ravindra *et al*., 2008).

Table 4: Component loadings obtained from principal component (PC) analysis

Variables	**Components**			
	PC1	**PC2**	**PC3**	**PC4**
Npt	-0.23	-0.23	0.20	-0.42
ANy	-0.21	-0.13	0.10	0.66
ANe	0.35	-0.20	0.16	-0.16
Fle	0.34	0.21	-0.04	0.12
Phe	0.08	0.37	-0.18	-0.34
Ant	0.14	0.09	-0.53	0.20
Flt	0.37	-0.14	0.06	0.00
Pyr	0.36	-0.12	0.12	-0.02
BaA	0.30	0.23	-0.12	-0.13
Chr	0.27	-0.13	0.02	0.08
BbF	0.08	0.37	0.26	0.07
BkF	0.00	0.06	0.66	-0.03
BaP	0.00	0.41	0.15	-0.13
BghiP	0.14	0.31	0.23	0.38
DBA	0.38	-0.13	0.06	0.04
IndP	-0.21	0.42	0.00	0.00
Eigenvalue	6.26	4.17	1.62	1.11
% of variance	39.15	26.06	10.12	6.96
Cumulative %	39.15	65.21	75.33	82.29
Probable sources	Coal & biomass combustion	Diesel & wood combustion	Diesel engines	Biomass & wood combustion

CONCLUSIONS

PAHs are ubiquitous in the environment due to their hydrophobic nature and affinity for particulate matter. PAHs are dominantly found in soil than other media. Besides emissions from atmospheric depositions, sludge / compost, and automobile workshops, their major sources in soils are various anthropogenic combustion activities. Therefore, PAHs has been reported in soils from various locations in developing India. However, literature on PAHs in environmental matrices from Gwalior city, India is scanty, which has been listed among the most polluted cities by World Health Organization. Traffic, open waste burning and industrial activities in the vicinity as major sources of air pollution have been reported

for polluted air quality of the city. No study is available on source of PAHs in any matrix for this region. During this study, possible sources of priority 16PAHs were explored using various diagnostic indices.
During study. it was observed that the concentrations ∑PAHs observed in Gwalior soils were much lower than reported PAHs in soils from various locations in other countries. The obtained results are comparable with the other cities in India. 3-ring PAHs (42%) and 4**-** ring PAHs (32%) were the most abundant in the soils, and indicated mixed pyrogenic sources. Marginally higher levels of ∑HMW-PAHs, and consequently low ratio of LMW to HMW PAHs suggested pyrogenic origin. Characteristic ratios of selected PAHs were used to identify the possible sources of PAHs, and their results suggested pyrogenic sources from vehicles, diesel engines, gasoline, fossil fuel combustion and biomass combustion as major sources of PAHs. Further, Pearson's correlation coefficient demonstrated the mixed pyrogenic sources including biomass and coal combustion and vehicular emissions as most significant sources of PAHs. Furthermore, PC analysis also attributed coal, wood and biomass combustion, and diesel engines as major sources of PAHs. Therefore, study concluded that mixed pyrogenic sources could be the most significant sources of PAHs in the soils from the city of Gwalior in central India.
However, Government of India has undertaken various initiatives in the recent past for the improvement of the environmental condition in India with mitigation of air pollution. Those initiatives include National Clean Air Programme, phasing out on old vehicles, stringent emission standards, metro rail transit system, mandatory use of CNG in public transportation, switched over coal-based power plants to gasoline, reduction of benzene in gasoline and improvement of fuel quality standards (MoEF & CC, 2019). As there are scarce reports on persistent organic pollutants for the central India, further comprehensive studies on these pollutants impact are warranted.

ACKNOWLEDGEMENTS

The authors are grateful to competent authorities of Central Pollution Control Board for providing the necessary facilities to conduct study. The views expressed in this paper are those of authors and do not necessarily reflect the organization's.

REFERENCES

Aleksandra UJ, Smreczak B, Agnieszka KP (2019). Soil organic matter composition as a factor affecting the accumulation of polycyclic aromatic hydrocarbons. *Journal of Soils and Sediments* **19** 1890–1900.

ATSDR (Agency for Toxic Substances and Disease Registry) (1995). Toxicological profile for polycyclic aromatic hydrocarbons (PAHs). US Department of Health and Human Services, Public Health Service. Atlanta, GA. [Online]. Available: http://www.atdsr.cdc.gov/toxpro.les/phs69 [Accessed 30 January 2020].

Bassey UL, Okeke PN, Ezichi MI, Njionye UO, Nwoko CO, Ebe TE (2019). Assessment of the Contamination Level of Polycyclic Aromatic Hydrocarbons in the Soil around Ekeatai River, Eket, Akwa Ibom State, Nigeria. *Applied Ecology and Environmental Sciences* **7**(6) 270-277.

Bosetti C, Boffetta P, La Vecchia C (2007). Occupational exposures to polycyclic aromatic hydrocarbons, and respiratory and urinary tract cancers: a quantitative review to 2005. *Annals of Oncology* **18** 431–446.

Cao W, Yin L, Zhang D, Wang Y, Yuan J, Zhu Y, Dou J (2019). Contamination, sources, and health risks associated with soil PAHs in rebuilt land from a coking plant, Beijing, China. *International Journal of Environmental Research and Public Health* **16** (4): 670.

Chen YG, Sheng GY, Bi XH (2005). Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environmental Science and Technology*, **39** 1861–1867.

Cusworth DH, Mickley LJ, Sulprizio MP, Liu T, Marlier ME, DeFries RS, Guttikunda SK, Gupta P (2018). Quantifying the influence of agricultural fires in northwest India on urban air pollution in Delhi, India. *Environmental Research Letters* **13** (4) 044018.

Dabaibeh RN (2020). Polycyclic aromatic hydrocarbons in topsoil: emergent trends in environmental assessment. *EurAsian Journal of BioSciences* **14** (1) 1427-1436.

Devi NL, Yadav IC, Shihua Q, Dan Y, Zhang G, Raha P (2016). Environmental carcinogenic polycyclic aromatic hydrocarbons in soil from Himalayas, India: Implications for spatial distribution, sources apportionment and risk assessment. *Chemosphere* **144** 493-502.

Deelaman W, Pongpiachan S, Tipmanee D, Choochuay C, Iadtem N, Suttinun O, Wang Q, Li X, Li G, Han Y, Hashmi MZ, Cao J. (2020). Source identification of polycyclic aromatic hydrocarbons in terrestrial soils in Chile. *Journal of South American Earth Sciences* **99**102514.

Dickhut RM, Canuel EA, Gustafson KE, Liu K, Arzayus, KM, Walker SE, Edgecombe G, Gaylor MO, MacDonald EH (2000). Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay Region. *Environmental Science and Technology* **34** (21) 4635–4640.

Dandotiya B, Jadon N, Sharma HK (2019). Effects of meteorological parameters on gaseous air pollutant concentrations in urban area of Gwalior City, India. *Environmental Claims Journal* **31**(1) 32-43.

DPES (Department of Planning, Economics and Statistics) (2016). Government of Madhya Pradesh [Online]. Available: http://des.mp.gov.in/en-us/Information-Technology [Accessed 30 January 2020].

EC (European Community) (2001). The list of priority substances in the field of water policy and amending directive, Council directive 2455/2001/ECC. Official Journal **L331**,1-5.

Enrique GF, Fernando TW, Diana DRM, **Heriberto EG (2016)**. Polycyclic aromatic hydrocarbons in road-deposited sediments and roadside soil in Tijuana, Mexico. *Soil and Sediment Contamination: An International Journal* **25**(2) 223-239.

Ghosh SP, Maiti SK (2020). Evaluation of PAHs concentration and cancer risk assessment on human health in a roadside soil: A case study. *Human and Ecological Risk Assessment: An International Journal* **26**(4) 1042-1061.

Gupta H, Kumar R (2020). Distribution of selected polycyclic aromatic hydrocarbons in urban soils of Delhi, India. *Environmental Technology and Innovations* **17** 100500.

Gurbani D, Bharti SK, Kumar A, Pandey AK, Ana GR, Verma A, Khan AH, Patel DK, Mudiam MK, Jain SK, Roy R, Dhawan A (2013). Polycyclic aromatic hydrocarbons and their quinones modulate the metabolic profile and induce DNA damage in human alveolar and bronchiolar cells. *International Journal of Hygiene and Environmental Health* **216**(5)553-65.

Hafner WD, Carlson DL, Hites RA (2005). Influence of local human population on atmospheric polycyclic aromatic hydrocarbon concentrations. *Environmental Science and Technology* **39** 7374–7379.

Herbstman JB (**2012**). Prenatal exposure to polycyclic aromatic hydrocarbons, Benzo[a]pyrene–DNA adducts, and genomic DNA methylation in cord blood. *Environmental Health Perspectives* **120** (5) 733-738.

IARC (International Agency for Research on Cancer) (2006). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol. 92, Lyone, France [Online]. Available: https://monographs.iarc.fr/monographs-available [Accessed 30 Januray 2020].

Katsoyiannis A, Terzi E, Cai QY (2007). On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? *Chemosphere* **69** 1337–1339.

Kaur S, Senthilkumar K, Verma VK, Kumar B, Kumar S, Katnoria JK, Sharma CS (2013). Preliminary analysis of polycyclic aromatic hydrocarbons in air particles (PM_{10}) in Amritsar, India: sources, apportionment, and possible risk implications to humans. *Archives of Environmental Contamination and Toxicology* **65** 382–395.

Kavouras JG, Koutrakis P, Tsapakis M, Lagoudaki E, Stephanou EG, Von Baer D, Oyola P (2001). Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. *Environmental Science and Technology* **35** 2288–2294.

Khalili NR, Scheff PA, Holsen TM (1995). PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric Environment* **29** 533-542.

Khillare PS, Hasan A, Sarkar S (2014). Accumulation and risks of polycyclic aromatic hydrocarbons and trace metals in tropical urban soils. *Environmental Monitoring and Assessment* **186**(5) 2907-2923.

Khanna I, Khare M, Gargava P and Khan AA (2018). Effect of PM2.5 chemical constituents on atmospheric visibility impairment. *Journal of the Air & Waste Management Association* **68**(5) 430-437.

Kumar B, Verma VK, Kumar S, Sharma CS (2014a). Polycyclic aromatic hydrocarbons in residential soils from an Indian city near power plants area and assessment of health risk for human population. *Polycyclic Aromatic Compounds* **34** (3) 191-213.

Kumar B, Verma VK, Mishra M, Kumar S, Sharma CS, Akolkar AB (2014b). Persistent organic pollutants in residential soils of North India and assessment of human health hazard and risks. *Toxicology and Environmental Chemistry* **96**(2)255-272.

Kumar B, Verma VK, Tyagi J, Sharma CS, Akolkar AB (2015a). Health Risk Due to Sixteen PAHs in Residential Street Soils from Industrial Region, Ghaziabad, Uttar Pradesh, India. *Journal of Environment Protection and Sustainable Development* **1** (2)101-106.

Kumar B, Verma VK, Sharma CS, Akolkar AB (2015b). Estimation of toxicity equivalency and probabilistic health risk on lifetime daily intake of polycyclic aromatic hydrocarbons from urban residential soils. *Human and Ecological Risk Assessment: An International Journal* **21**(2)434-444.

Kumar B, Verma VK, Tyagi J, Sharma CS, Akolkar AB (2016). Occurrence and Source Apportionment of Polycyclic Aromatic Hydrocarbons in Urban Residential Soils from National Capital Region, Uttar Pradesh, India. *Polycyclic Aromatic Compounds* **36**(5) 729-744.

Lee WJ, Wang YF, Lin TC, Chen YY, Lin WC, Ku CC, Cheng JT (1995). PAH characteristics in the ambient air of traffic-source. *Science of The Total Environment* **159** 185-200.

Li G, Sun GX, Ren Y, Lu XS, Zhu YG (2018). Urban soil and human health: a review. *European Journal of Soil Science* **69** 196-2015.

Liu Y, Gao P, Su J, da Silva EB, de Oliveira LM, Townsend T, Xiang P, Ma LQ (2019). PAHs in urban soils of two Florida cities: Background concentrations, distribution, and sources. *Chemosphere* **214** 220-227.

MoEF & CC (2019). Various initiatives undertaken by Government of India for mitigation of air pollution [Online]. Available: https://pib.gov.in/newsite/PrintRelease.aspx?relid=194865 [Accessed 30 January 2020].

Islam MN, Jo YT, Chung SY, Park JH (2018). Assessment of Polycyclic aromatic hydrocarbons in school playground soils in urban Gwangju, South Korea. *Archives of Environmental Contamination and Toxicology* **74**(3) 431-441.

Perera FP, Wang S, Vishnevetsky J, Zhang B, Cole KJ, Tang D, Rauh V, Phillips DH (**2011**)**.** Polycyclic aromatic hydrocarbons–aromatic DNA adducts in cord blood and behavior scores in New York city children. *Environmental Health Perspectives* **119** (8) 1176-1181.

Pokhrel B, Gong P, Wang X, Chen M, Wang C, Gao S (2018). Distribution, sources, and air-soil exchange of OCPs, PCBs and PAHs in urban soils of Nepal. *Chemosphere* **200** 532-541.

Prasse C, Zech W, Itanna F, Glaser B (2012). Contamination and source assessment of metals, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in urban soils from Addis Ababa, Ethiopia. *Toxicological and Environmental Chemistry* **94** (10)1954-1979.

Raissa AO, Wewers F, Ikhide PO, Farrar T, Giwa AR (2017). Spatio–temporal distribution of polycyclic aromatic hydrocarbons in urban soils in Cape Town, South Africa. *International Journal of Environmental Research* **11** 189–196.

Ravindra K, Sokhi R, Grieken RV (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment* **42** (13) 2895-2921.

Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT (1993). Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environmental Science and Technology* **27** 1892–1904.

Saba B, Hashmi I, Awan MA, Nasir H and Khan SJ (2012). Distribution, toxicity level, and concentration of polycyclic aromatic hydrocarbons (PAHs) in surface soil and groundwater of Rawalpindi, Pakistan. *Desalination and Water Treatment* **49**(1-3) 240-247.

Schroeder H (2011). Developmental Brain and Behavior Toxicity of Air Pollutants: A focus on the effects of polycyclic aromatic hydrocarbons (PAHs). *Critical Reviews in Environmental Science and Technology* **41**(22) 2026-2047.

Sharma HK, Ahamad I, Jadon N (2016). Assessment of ambient air quality with special reference to NOx and its health impacts on local population in Gwalior city, Madhya Pradesh, India. *Research Journal of Chemical & Environmental Sciences* **4**(3)|79-87.

Sharma HK, Dandotiya B, Jadon N (2017). Exposure of air pollution and its health effects in traffic police persons of Gwalior city, India. *Environmental Claims Journal* **29** (4)305–15.

Simcik MF, Eisenreich SJ, Lioy PJ (1999). Source apportionment and source/sink relationship of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmospheric Environment* **33** 5071–5079.

Singh DP, Gadi R, Mandal TK (2012). Levels, sources, and toxic potential of polycyclic aromatic hydrocarbons in urban soil of Delhi, India. *Human and Ecological Risk Assessment: An International Journal* **18**(2)393-411.

Suman S, Sinha A, Tarafdar A (2016). Polycyclic aromatic hydrocarbons (PAHs) concentration levels, pattern, source identification and soil toxicity assessment in urban traffic soil of Dhanbad, India. *Science of the Total Environment* **545–546** 353–360.

Tarafdar A, Sinha A (2019). Health risk assessment and source study of PAHs from roadside soil dust of a heavy mining area in India. *Archives of Environmental & Occupational Health* **74**(5)252-262.

2015. Appendix A to 40 CFR, Part 423–126 Priority Pol-

lutaUSEPA (United States Environmental Protection Agency). 2015. Appendix A to 40 CFR, Part 423–126 Priority Pollutants. Accessed 30.01.2020, https://www.gpo.gov/fdsys/ pkg/CFR-2018-title40-vol31/pdf/CFR-2018-title40- vol31-part423-appA.pdf

USEPA Method 3550C [Online]. Avaliable: https://www.epa.gov/sites/production/files/2015-12/documents/3550c.pdf [Accessed 30 January 2020]

USEPA Method 3630C [Online]. Available: https://www.epa.gov/sites/production/files/2015-12/documents/3630c.pdf [Accessed 30 January 2020]

USEPA (United States Environmental Protection Agency) (2015). Appendix A to 40 CFR, Part 423–126 Priority Pollutants. Accessed 30.01.2020, https://www.gpo.gov/fdsys/pkg/CFR-2018-title40-vol31/pdf/CFR-2018-title40-vol31-part423-appA.pdf

Wang HK, Chen KS, Lu JJ, Peng YP, Wang WC, Tsai MY, Lai CH (2007). Dry deposition of airborne particles and characteristics of polycyclic aromatic hydrocarbons in urban Kaohsiung, Taiwan. *Aerosol and Air Quality Research* **7** 106-120.

Wang Z, Ma X, Na G, Lin Z, Ding Q, Yao Z (2009). Correlations between physicochemical properties of PAHs and their distribution in soil, moss and reindeer dung at Ny-Ålesund of the Arctic. *Environmental Pollution* **157** 3132–3136.

WHO (World Health Organization) (2018). WHO global urban ambient air pollution database (Update 2018) [Online]. Available: https://www.who.int/airpollution/data/cities/en/ [Accessed 30 January 2020].

Williams ES, Mahler BJ, Metre PC (2013). Cancer risk from incidental ingestion exposures to PAHs associated with coal-tar-sealed pavement. *Environmental Science and Technology* 47 (2) 1101–1109.

Wilcke W (2007). Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. *Geoderma* **141** 157–66.

Wu J, Li K, Ma D, Yu, Chai C (2018). Contamination, source identification, and risk assessment of polycyclic aromatic hydrocarbons in agricultural soils around a typical coking plant in Shandong, China. *Human and Ecological Risk Assessment: An International Journal* **24 (**1) 225-241.

Yunker MB, Macdonald RW, Vingarzan R, Mitchell HR, Goyette D, Sylvestre S (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* **33** 489–515.