Profile of Atmospheric PAHs in Rawalpindi, Lahore and Gujranwala Districts of Punjab Province (Pakistan)

Atif Kamal[1*], Jabir Hussain Syed[2], Jun Li[2], Gan Zhang[2], Adeel Mahmood[1], Riffat Naseem Malik[1]

[1] *Environmental Biology and Ecotoxicology Laboratory, Department of Environmental Sciences, Faculty of Biological Sciences, Quaid-i-Azam University, Islamabad, 45320, Pakistan*
[2] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

ABSTRACT

In this study, polyurethane foam passive air samplers (PUF-PAS) were deployed to evaluate the atmospheric concentration levels and ambient exposure of polycyclic aromatic hydrocarbons (PAHs) in Gujranwala, Lahore and Rawalpindi districts of the Punjab Province (Pakistan). The PAHs were extracted from the PUFs disks using Soxhlet extraction assembly, and were further concentrated using rotary evaporator, purified on a column, packed with alumina/silica, and eluted with a solution of dichloromethane:hexane (1:1 v:v). The PAHs quantification was carried out gas-chromatograph equipped with a mass-spectrometer (GC-MS). Regression scatter plots and molecular diagnostic ratios were used to identify and characterize the emission of PAH species from different sources. Among all detected PAHs, a high concentration of naphthalene (Naph) was observed in Lahore (327 pg m^{-3}) and Rawalpindi (316 pg m^{-3}) cities followed by phenanthrene, banzo(a)pyrene, pyrene, benzo(b)florenthene and benzo(k)flourenthene. Our findings revealed that the low molecular weight (LM)-PAHs in Rawalpindi and Gujranwala cities could have possibly originated from a local petroleum refinery and vehicular emissions respectively, whereas the high molecular weight (HM)-PAHs observed in Wazirabad, could be largely related to both biomass and traffic emissions. Results also showed that ~88 percent of the atmospheric PAHs could be attributed to the wood combustions (R^2 = 0.88), out of which more than 50 percent of wood combustion were possibly with the brick kiln sector (R^2 = 0.53).

Keywords: Environmental pollution; ILCR; Exposure; Pakistan; PAHs.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are well known for their adverse health outcomes in human. Recently, PAHs have been included in Convention on Long-range Tranboundary air pollution on persistent organic pollutants (POPs) (UNEC, 1998) and are widely studied by scientific community because of being among the group of first possible carcinogenic pollutants (WHO/IPCS, 1998; Kamal *et al.*, 2015a). The discovery of mutagenic and carcinogenic properties of several PAHs have brought them under the serious consideration of scientific community (Nisbet and LaGoy, 1992; Taioli *et al.*, 2007). Although there are hundred of different PAH congeners but U.S. EPA selected 16 PAH congeners as "priority pollutants" in 1970s (Nisbet and

LaGoy, 1992; Kamal *et al.*, 2014). Since the PAHs with high molecular weight possess carcinogenic proprieties, they have been categorized as confirm carcinogen (Class-1), probable carcinogenic (2A) or possible carcinogenic (2B) to human (IARC, 1983, 1987; Shi *et al.*, 2005; Kamal *et al.*, 2014). In all over the world (e.g., USA, European Union, China, Italy, UK), permissible limits of BaP emissions have been introduced to control PAHs emissions (Wu *et al.*, 2014 and reference therein), however there is a wide gap in PAHs control in some developing countries.

PAHs that originate either from anthropogenic activities such as combustion processes can be easy inhaled and ingested by human being (Simcik *et al.*, 1998; Lohmann *et al.*, 2000). A large amount of PAHs are released during incomplete combustion of organic materials (Zhang and Tao, 2009; Ma *et al.*, 2010). Similarly, as the combustion of fuel in the automobiles, account for ~5% and domestic coal account for ~4%, globally, while industrial emission remains < ~10%. The country-wide frequencies of biomass and fuel consumption vary with their economic conditions and population. For instance, the biofuel is a major source

---

* Corresponding author.
  Tel./Fax: +9205190643017
  E-mail address: r_n_malik2000@yahoo.co.uk

of energy (~90%) in developing/rural regions of the world and accounts for a large proportion of PAHs emission (Zhang and Tao, 2009). The combustion of biomass material accounts for ~57% of global emission of PAHs. In addition to the combustion processes, the widespread distribution of the atmospheric PAHs is also facilitated by their physico-chemical properties, e.g., low reactivity and vapor pressure, (Nam *et al.*, 2003).

Some studies conducted in the developing countries have demonstrated that the urban PAHs concentrations were higher than those in the surrounding rural areas; however, due to insufficient data from such regions (Li *et al.*, 2014), the conclusion remains largely immature. There is a dire need to monitor PAHs emissions in the developing countries like Pakistan, where such phenomenon is not studied extensively. In Pakistan there is only one study on the concentration of atmospheric PAHs available so far, (i.e., Smith *et al.*, 1995), in which the environmental PAH monitoring was conducted at three sites in Lahore city of Pakistan. The study, was based on the results of an active sampling device, which showed that the concentration of PAHs was quite high and comparable to those in some Indian cities. However, no detailed study was ever conducted in this reagion everafter. In recent years, the passive air samplers (PAS) based on sorbent disks of polyurethane foam housed in stainless steel protective chambers are widely used for the sampling of atmospheric persistent organic pollutants. These devices do not require any electric pump and can be installed in many sites, and provide high retention capacity for many organic compounds (Harner *et al.*, 2004; Choi and Spengler *et al.*, 2014).

The use of PAS device to monitor POPs concentration levels is of beneficial in the energy deficient countries like Pakistan where large proportion of energy (around ~27%) is derived from the combustion of biomass fuel (~76% of which is shared by household biomass use), and it is one of the countries of the world where biomass utilization is increasing at the rate of ~2% per annum (Butt *et al.*, 2013). It is expected that due to the lack of sound pollution control planning in some major cities of Pakistan (i.e., Lahore, and Rawalpindi) (von Schneidemesser *et al.*, 2010), emissions are largely associated with traffic exhaust and high influx of heavy traffic and the problem will continue to increase in the future. In addition to traffic pollution, in cities like Gujranwala and adjacent towns (i.e., Sohdra, and Wazirabad) they are also facing high pressure of industrial as well as conventional fossil fuel combustion activities in the residential areas.

Considering the above discussed scenario, this study was designed to evaluate the concentration of atmospheric PAHs in three highly populated districts (i.e., Rawalpindi, Lahore and Gujranwala) of Punjab province (Pakistan). Moreover, source apportionment of the ambient PAHs was also performed and discussed.

MATERIALS AND METHODS

Deployment of Passive Air Samplers for PAH Monitoring

The PUF disks housed in a stainless steel protective air sampling device chambers were installed in various stations. The PUF disks (having a diameter of 14 cm, 1.3 cm thickness, and 0.02 g cm^{-3} density) were wrapped in a sterile aluminum foil and sealed in zip-lock bags for transportation to the sampling sites. For PAHs monitoring in ambient air, several stations were selected in the major cities which were under surveillance in this study. We deployed PAS in three districts for consecutive 56-days periods (Fig. 1).

Rawalpindi and Islamabad are twin-cities and far away from rest of the cities and are surrounded by neighboring Margallah-Hills, and represent less polluted areas of urban/sub-urban population. The Wazirabad, Sohdra are small towns within the district Gujranwala, and are surrounded by the rural areas, while Lahore is a very old and one of the mega cities of Pakistan. For comparison, the districts were classified into three zone based on the known anthropogenic activities in these areas; these zones were classified as zone-A (Rawalpindi and Islamabad twin cities) where there is no extensive industrial or agricultural activities, zone-B (Gujranwala, Sohdra and Wazirabad) the zone is characterized by agricultural and industrial activities, zone-C (Lahore city) the zone represents districts and popular cities with high-traffic pollution and industrial activities.

Sample Preparation, Extraction, Clean-up and Analyses

PAHs were extracted from the PUFs disks using Soxhlet extraction assembly. The extraction was carried out using the dichloromethane (DCM) for 24 h. After 24 h, the resultant extracts were further concentrated using rotary evaporator and purified on a column, packed with alumina/silica. The elution was carried out with a solution of DCM:Hexane (1:1 v:v) and then elute was blown down under gentle stream of nitrogen to 25 µL. We used hexamethylbenzene in dodecane (1000 ng) as an internal standard before the analytical phase. We quantified 16-EPA priority PAHs including acenapthene (Ace), acenapthylene(Acy), anthracene (Ant), benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(g,h,i)perylene (BghiP), benzo(k)fluoranthene (BkF), chrysene (Chry), dibenzo(a,h)anthracene (DBA), fluoranthene (Fla), fluorene (Fl), indeno(1,2,3-c,d)pyrene (IP), naphthalene (Naph), phenanthrene (Phe) and pyrene (Pyr).

The analysis of PAHs in each sample was carried out using 1 µL (in split less mode, and 10 min solvent delay time) on the Gas-chromatograph (Agilent 7890) equipped with a capillary column (DB-5MS, 30 m, 0.25 mm, and 0.25 µm) and a mass-spectrometric detector and (Agilent 5975-Mass Selective-Detector). The temperature of the oven was initially 60°C, for one minutes, and was then raised up to 290°C (rate of change was 3 °C min^{-1} held for 20 min). The temperature of transfer lines and that of the injector was 300°C and 290°C respectively. The mobile phase used was a carrier gas (high purity helium, with a flow rate of 1.83 mL min^{-1}).

Quality Control and Quality Assurance (QC/QA)

To ensure good accuracy and analytical precision, the PAHs standards were run on daily basis, which showed that the average standard deviation of the instrument analyses was equal or less than ± 10%. The PUFs samples were spiked with
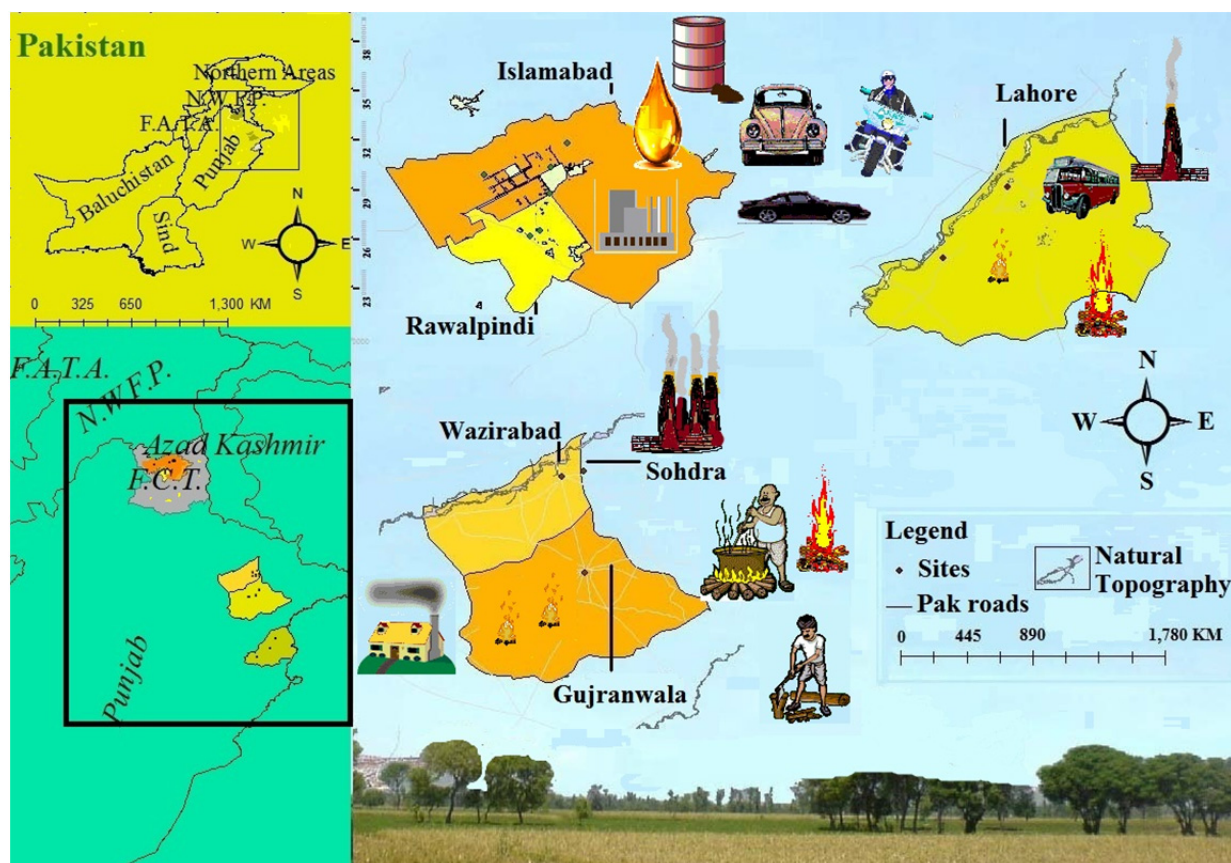
Fig. 1. Sampling sites (cities) in Punjab province, Pakistan.

1000 ng of deuterated PAHs (3–5 replicates). The recovery standards used (including the chrysene-D_{12}, perylene-D_{12}, acenapthene-D_{10} and phenanthrene-D_{10}), ranged between 76% and 87%. The recovery percentage of deuterated PAHs ranged between 76 and 87%, while that of surrogate-PAHs was $93 \pm 13\%$ for benzo(a)pyrene-d^{12}, $97 \pm 12\%$ for fluoranthene-d^{10}, $94 \pm 11\%$ for *p*-therpenyl-d^4. We also analyzed the field blank samples (a set of 6-field blanks) to eliminate the chances of background contamination. The method detection limits (MDLs) were the average values of the blanks, $\pm$ 3 times the standard deviations of the blanks. Three times of the instrumental detection limit (IDL) were used for calculating the MDLs. The IDL values were calculated using the lowest standards and extrapolating to the corresponding amount of analyte that generates a signal-to-noise ratio of 3:1. All target compounds detected in the samples, and lab-blanks were under the IDLs. The data reported in this study were not corrected by the recoveries.

Coefficient of Divergence

The coefficient of divergence (CD) was used to identify the similarities between the profiles of PAHs at two different sites (e.g., city wise comparison). The generic formulae used for CD calculation was as follows

$$CD(jk) = \left[1/P \sum_{i=1}^{p} \left(\frac{Xij - Xik}{Xij + Xik} \right)^{1/2} \right] \qquad (1)$$

The *j*, and *k* represent profile of PAHs in tow different sampling sites, *p* shows the number of target compounds, x is the average concentration of the component (Wongphatarakul *et al.*, 1998). The value of CD < 0.269 reflects a probable divergence between particles between two cities/zones, a CD value > 0.16 suggests a commons source in two sites under discussion (Wongphatarakul *et al.*, 1998).

Statistical Analysis

All the concentrations of individual and total PAHs detected in air samples and diagnostic ratios calculated for source identification have been presented as mean $\pm$ standard deviation, median, minimum and maximum values while all the PAHs results have been presented in pg m^{-3}. Sampling sites were divided into 3 zones (represented three districts i.e., zone-A, B and C) based on hypothesized low medium and high levels of pollution in different cities. Numerical data was also tested for any deviation from normality using the Kolmogorov-Smirnov (K-S) normality test. Comparative analysis was performed using independent samples t-test among cities/zones. All statistical analyses were performed using MS-Excel and SPSS statistical software (version 20.0).

RESULTS AND DISCUSSION

Atmospheric PAH Profile

The individual and total concentrations of 16-PAHs (Fig. 1) have been summarized in Table 1–4. The PAHs

Table 1. Diagnostic ratios and the concentrations of individual and total PAHs in the atmosphere of three sampling zones (Punjab).

PAHs (ring#) (Abbrev) TEFs	Zone–A (residential) RW Mean ± S.dev Med	Min–Max	Zone–B (industrial/agri) GJ Mean ± S.dev Med	Min–Max	Zone–C (industrial/traffic) LR Mean ± S.dev Med	Min–Max	*p*–values AB (1.07)*	AC (1.71)*	BC (0.55)*
Naphthalene (3) (Naph) 0.001	289 ± 35 288	248–339	327 ± 18 328	325–329	292 ± 59 272	229–372	0.11	0.90	0.34
Acenaphthene (3) (Ace) 0.001	9 ± 14 3	2–37	14 ± 4 14	13–15	9 ± 3 10	4–13	< 0.01	0.002	0.6
Acenaphthylene (3) (Acy) 0.001	4 ± 1 4	3–6.2	10 ± 4 10	9–12	9 ± 2 9	6–14	0.54	0.97	0.03
Anthracene (3) (Ant) 0.01	13 ± 4 12	1–26	6.7 ± 1 7	5–9	36 ± 14 32	20–57	< 0.001	< 0.001	0.4
Fluorene (3) (Fl) 0.001	15 ± 3 14	8–25	57 ± 18 57	56–57	49 ± 14 47	31–66	0.67	0.12	0.2
Phenanthrene (3) (Phe) 0.001	177 ± 11 173	166–198	174 ± 2 174	165–176	171 ± 5 169	164–178	0.27	0.004	0.2
Benzo(a)anthracene (4) (BaA) 0.1	237 ± 9 233	229–255	246 ± 12 245	234–247	234 ± 13 230	219–252	0.85	0.84	0.006
Chrysene (4) (Chry) 0.01	157 ± 47 154	112–323	335 ± 12 335	334–336	169 ± 95 168	134–341	0.34	0.08	0.87
Fluoranthene (4) (Fla) 0.001	267 ± 6 264	261–281	267 ± 15 266	266–270	267 ± 3 267	265–270	0.4	0.76	0.94
Pyrene (4) (Pyr) 0.001	188 ± 86 280	nd–289	276 ± 1 278	275–277	276 ± 3 278	270–280	0.08	0.9	0.03
Benzo(a)pyrene (5) (BaP) 1	Nd	Nd	283 ± 122 149	nd–498	143 ± 64 141	nd–292	–	–	0.33
Benzo(b)fluoranthene (5) (BbF) 0.1	305 ± 9 302	299–322	300 ± 15 301	299–301	199 ± 5 299	199–301	0.56	0.47	0.28
Benzo(k)fluoranthene (5) (BkF) 0.1	268 ± 72 317	213–336	315 ± 2 315	315–317	211 ± 8 315	115–318	0.6	0.62	0.27
Dibenzo(a,h)anthracene (5) (DBA) 1	37 ± 13 19	16–129	7 ± 2 7	6–8	34 ± 11 20	6–8	0.69	0.45	0.046
Indeno(1,2,3,c,d)pyrene (6) (IP) 0.1	47 ± 19 27	14–168	17 ± 1 17	16–19	52 ± 21 49	15–91	0.4	0.87	0.09
Benzo(ghi)perylene (6) (BghiP) 0.01	22 ± 12 22	7–78	4 ± 1 4	3–5	18 ± 2 10	3–28	0.3	0.76	0.039
∑PAHs	2178 ± 571 2023	1631–2894	2359 ± 7 2360	2351–2366	2038 ± 481 2393	1375–2430	0.6	0.89	0.3
∑COMB	1233 ± 524 1498	1120–2326	1763 ± 45 1764	1755–1770	1438 ± 229 1773	837–1796	0.8	0.13	0.26
∑7Carcinogens	1009 ± 426 1024	855–1174	1160 ± 5 1160	1155–1164	1088 ± 116 1169	568–1531	0.85	0.59	0.77
IP/(IP+BghiP)	0.7 ± 0.04 0.68	0.67–0.79	0.7 ± 0.03 0.73	0.69–0.77	0.79 ± 0.06 0.81	0.69–0.86	0.2	0.01	0.03
Fla/(Fla+Pyr)	0.66 ± 0.3 0.49	0.49–1	0.4 ± 0.2 0.49	0.2–0.5	0.49 ± 0.1 0.49	0.49–0.59	0.09	0.15	0.32

*= values of Coefficient of divergence.
TEF for individual PAHs relative to BaP as reported by Nisbet and LaGoy (1992), except TEF values for Cor and BeP which were adopted from the studies of Malcom and Dobson (1994); *p* = probability value, α = 0.05; ∑PAHs = sum of non–alkylated 16-PAHs.
∑COMB = Sum total of combustion origin PAHs i.e., BaA, BaP, BbkF, BeP, BghiP, Chry, Fla, IP, Pyr (Prahl and Carpenter, 1983).
∑7Carcinogenic PAHs = BaA, BaP, BbkF, BghiP, IP, Pyr; LM-PAHs = low molecular weight PAHs; HM-PAHs = high molecular weight PAHs.
Zone–A = Rawalpindi (RW), Zone–B = Lahore (LR); Zone–C = Gujranwala (GJ).

Table 1. (*continued*).

PAHs (ring#) (Abbrev) TEFs	Zone–A (residential) RW		Zone–B (industrial/agri) GJ		Zone–C (industrial/traffic) LR		*p*–values		
	Mean ± S.dev Med	Min–Max	Mean ± S.dev Med	Min–Max	Mean ± S.dev Med	Min–Max	AB (1.07)*	AC (1.71)*	BC (0.55)*
Ant/(Phe+Ant)	0.07 ± 0.04 0.06	0.01–0.13	0.20 ± 0.05 0.20	0.16–0.25	0.07 ± 0.04 0.08	0.03–0.12	0.001	0.82	0.001
BaP/(BaP+Chry)	0.7 ± 0.3 0.62	0.43–1	1 ± 0.05 1	0.1–12	0.4 ± 0.09 0.42	0.4–0.43	0.01	0.03	< 0.01
Fl/(Pyr+Fl)	0.4 ± 0.2 0.07	0.03–1.1	0.17 ± 0.03 0.17	0.14–0.2	0.14 ± 0.04 0.14	0.1–0.17	0.34	0.3	0.08
Σ COMB/ΣPAHs	0.7 ± 0.05 0.74	0.69–0.8	0.67 ± 0.07 0.66	0.6–0.74	0.7 ± 0.1 0.74	0.7–0.75	0.06	0.84	0.01

concentrations (∑PAHs) ranged between 1375 and 1398 pg m^{-3} (in Sohdra) > from 2108 to 2894 pg m^{-3} in the Lahore city. The ∑PAHs and total combustion origin-PAHs (∑COMB-PAHs) were relatively high in the Lahore (2621 pg m^{-3} and 2026 pg m^{-3}) followed by Gujranwala (2397 pg m^{-3} and 1778 pg m^{-3}) > Rawalpindi (2359 pg m^{-3} and 1763 pg m^{-3}) > Wazirabad (2332 pg m^{-3} and 1698 pg m^{-3}) > Sohdra (1389 pg m^{-3} and 841 pg m^{-3}) > Islamabad (1735 pg m^{-3} and 124 pg m^{-3}). The ∑7-carcinogenic PAHs were also highly prevalent in the Lahore (1549 pg m^{-3}) followed by Wazirabad (1523 pg m^{-3}) > Gujranwala (1169 pg m^{-3}) > Rawalpindi (1161 pg m^{-3}) > Islamabad (870 pg m^{-3}) > Sohdra (574 pg m^{-3}). The high concentration of ∑7-carcinogenic PAHs (ranging between 569 and 579 (pg m^{-3}) were observed in Sohdra, and those ranging between 1171 and1743 (pg m^{-3}) were observed in Lahore city. Since the high load of pollution in zone-B and zone-C was expected, which could be correlated with the frequency of combustion emission from, firewood/coal, likewise, the sources such as heavy traffic exhaust and many other human activities remarkably contribute to atmospheric PAHs emission profile in these areas. In the urban regions, the vehicular exhaust emission, in particular, could be the most significant source of PAHs in the local environment (Ahmad *et al.*, 2012; Kamal *et al.*, 2014a, b).

PAHs Profile in the Atmosphere of the District Rawalpindi/Islamabad and Lahore

Among PAHs congeners, high concentration of Naph was observed in Lahore (327 pg m^{-3}) and Rawalpindi (316 pg m^{-3}) cities. PAH-congeners such as Phe, BaA, Pyr, BbF, BkF were dominant in Lahore > Rawalpindi > Islamabad. The concentration of the Naph was high in the Rawalpindi (317 pg m^{-3}), as compared to that in the Islamabad city (261 pg m^{-3}) (*p* = 0.03) (Table 2). The Naph (327 pg m^{-3}), Acy (10 pg m^{-3}) Fl (56 pg m^{-3}) BaA (246 pg m^{-3}) were also considerably higher in the Lahore city than those detected in the atmosphere of Islamabad. Lahore city is a densely populated and highly polluted because of old vehicular traffic. Lahore receives emissions from industrial activities, brick kilns, and use of coal/wood for cooking purposes in villages in the suburban towns. All these factors together contribute to the air pollution and the atmospheric PAHs emissions. In fact, according to World Health Organization

(WHO), the City Lahore is facing high level of organic carbon (OC) contents and the levels of particulate matter (PM) were above the WHO guidelines (Stone *et al.*, 2010). The PM bound OC in this city could be attributed to the combustion of biomass fuel and petroleum in motor vehicles (Stone *et al.*, 2010). In Lahore city; the passive sampling station was selected in the Chung Khurd area. In this area, the HM-PAHs such as IP, BghiP, BaA and DBA were observed in high concentration in the atmosphere of Lahore city, which could have originated from gasoline and diesel exhaust. The concentration of Phe, Fla, IP and BghiP is usually high in the vehicular emissions exhaust (de Andrade *et al.*, 2010). Similarly, other PAH congeners including the BghiP, Cor, Phe are also present in the motor vehicular exhaust emission (Ravindra *et al.*, 2006), moreover; the Phe was high in Rawalpindi and Lahore and high Pyr concentration in all three cities represent a mix contribution of anthropogenic origin (i.e., oil/biomass combustion and vehicular exhaust emission) in these cities (Ravindra *et al.*, 2008). In Lahore, high concentration of BghiP and IP indicated gasoline and oil combustion (Kwon and Choi, 2008). In addition, we observed high concentration of several LM-PAHs in Rawalpindi city, including Naph, Phe, which could be originating from the petroleum refinery located within the city suburbs, in particular, from the functional incinerator of this refinery which could be is a very important source of volatile PAHs and particulate matter (PM) in these areas (Kamal *et al.*, 2013, 2015b).

PAH Profile in the Atmosphere of District Gujranwala (Including Sohdra and Wazirabad Towns)

The results revealed that Naph (368 pg m^{-3}), Fla (270 pg m^{-3}), Phe (177 pg m^{-3}) were high in the atmosphere of Gujranwala city, than those in Sohdra town (236, 270, and 165 pg m^{-3} respectively), whereas other PAHs congeners were quiet higher in Sohdra town than in the atmosphere of Gujranwala (P < 0.05) except Pyr. The BaP, Bb + kF, Chry were not detected in the atmosphere of Sohdra; similarly, the BaP was not detected in the atmosphere of Gujranwala. In addition, the atmospheric concentration of PAHs in Wazirabad was also dominated by Naph (273 pg m^{-3}), Fl (66 pg m^{-3}), Ant (54 pg m^{-3}), IP (88 pg m^{-3}), DBA (54 pg m^{-3}), and BghiP (28 pg m^{-3}) and these congeners were significantly high (Tables 3 and 4). In general, LM-PAHs

Table 2. Concentration of individual PAH congeners detected in the atmosphere of Rawalpindi, Islamabad and Lahore cities of Punjab (Pakistan).

Sites	Rawalpindi		Islamabad		Lahore		Probabilities (P–value)		
PAHs (Abbrev) TEFs (ring #)	Mean ± S.dev / Med	Min–Max	Mean ± S.dev / Med	Min–Max	Mean ± S.dev / Med	Min–Max	RI	RL	IL
Naphthalene (Naph) 0.001 (3)	317 ± 23 / 317	294–39	261 ± 18 / 254	249–282	327 ± 42 / 327	325–329	0.03	0.5	0.03
Acenaphthene (Ace) 0.001 (3)	3 ± 1 / 2	2–4	15 ± 5 / 14	3–37	14 ± 1 / 14	13–15	0.35	< 0.001	0.96
Acenaphthylene (Acy) 0.001 (3)	4 ± 1 / 4	3–6	5 ± 1 / 5	4–6	10 ± 1 / 10	9–12	0.25	0.02	0.004
Anthracene (Ant) 0.01 (3)	16 ± 12 / 22	1–26	10 ± 4 / 9	8–15	7 ± 2 / 7	5–9	0.5	0.28	0.19
Fluorene (Fl) 0.001 (3)	16 ± 8 / 12	10–25	14 ± 5 / 16	8–18	56 ± 5 / 56	55–56	0.75	0.001	< 0.001
Phenanthrene (Phe) 0.001 (3)	184 ± 14 / 181	172–198	171 ± 3 / 172	167–175	175 ± 32 / 175	173–175	0.2	0.3	0.22
Benzo(a)anthracene (BaA) 0.1 (4)	239 ± 12 / 235	230–254	234 ± 7 / 231	229–241	246 ± 21 / 246	244–247	0.5	0.4	0.03
Chrysene (Chry) 0.01(4)	207 ± 67 / 212	96–312	108 ± 56 / 107	nd–323	335 ± 42 / 334	334–337	0.47	0.1	0.1
Fluoranthene (Fla) 0.001(4)	270 ± 9 / 266	264–281	262 ± 22 / 263	261–264	267 ± 22 / 268	266–270	0.2	0.6	0.03
Pyrene (Pyr) 0.001 (4)	283 ± 5 / 281	280–289	93 ± 16 / 92	91–279	277 ± 31 / 277	275–278	0.1	0.07	0.1
Benzo(a)pyrene (BaP) 1 (5)	Nd	Nd	Nd	Nd	283 ± 56 / 351	351–499	–	–	–
Benzo(b)fluoranthene (BbF) 0.1 (5)	311 ± 10 / 307	302–323	300 ± 2 / 300	299–302	300 ± 2 / 300	298–301	0.17	0.17	0.9
Benzo(k)fluoranthene (BkF) 0.1 (5)	326 ± 9 / 322	319–336	211 ± 81 / 316	315–317	316 ± 11 / 316	315–316	0.33	0.14	0.4
Dibenzo(a,h)anthracene (DBA) 1 (5)	19 ± 4 / 16	6–8	7 ± 1 / 7	17–129	56 ± 23 / 23	157–23	0.25	0.36	0.01
Indeno(1,2,3,c,d)pyrene (IP) 0.1 (6)	17 ± 2 / 17	14–29	21 ± 7 / 21	27–168	74 ± 42 / 28	16–19	0.29	0.32	0.4
Benzo (g,h,i)perylene (BghiP) 0.01 (6)	10 ± 3 / 10	3–5	4 ± 1 / 34	7–79	33 ± 19 / 13	7–14	0.27	0.38	0.04

TEF for individual PAHs relative to BaP as reported by Nisbet and LaGoy (1992), except TEF values for Cor and BeP which were adopted from Malcom and Dobson (1994); p = probability value, significant when < 0.05; $\sum$PAHs = sum of non-alkylated total PAHs.

$\sum$COMB = PAHs of combustion origin i.e., BaA, BaP, BbkF, BeP, BghiP, Chry, Fla, IP, Pyr (Prahl and Carpenter, 1983).

$\sum$7–Carcinogenic PAHs = BaA, BaP, BbkF, BghiP, IP, Pyr.

LMPAHs = low molecular weight PAHs; HMPAHs = high molecular weight PAHs; RI = Rawalpindi vs. Islamabad; RL; Rawalpindi vs. Lahore; IL = Islamabad vs. Lahore.

Table 3. Concentration of individual PAH congeners detected in the atmosphere of Sohdra, Gujranwala and Wazirabad cities of Punjab (Pakistan).

Sites	Sohdra		Gujranwala		Wazirabad		Probabilities (p–values)		
PAHs (ring #) (Abbreviations) TEFs	Mean ± S.dev Med	Min–Max	Mean ± S.dev Med	Min–Max	Mean ± S.dev Med	Min–Max	SG	SW	GW
Naphthalene (3) (Naph) 0.001	236 ± 6 / 237	229–241	368 ± 14 / 368	364–372	273 ± 26 / 273	270–276	< 0.001	0.001	< 0.001
Acenaphthene (3) (Ace) 0.001	12 ± 4 / 12	12–13	5 ± 0.4 / 5	4–5	10 ± 2 / 10	9–10	0.001	0.004	< 0.001
Acenaphthylene (3) (Acy) 0.001	13 ± 1 / 13	12–14	6 ± 1 / 6	5.9–6.9	9 ± 0.03 / 9	8–9.3	< 0.001	0.002	0.001
Anthracene (3) (Ant) 0.01	32 ± 21 / 32	31–33	22 ± 1 / 22	21–24	54 ± 19 / 54	51–57	0.001	< 0.001	< 0.001
Fluorene (3) (Fl) 0.001	48 ± 1 / 48	47–49	32 ± 1 / 32	31–32.9	66 ± 6 / 66	65–66	< 0.001	< 0.001	< 0.001
Phenanthrene (3) (Phe) 0.001	166 ± 11 / 166	165–167	177 ± 21 / 177	175–178	168 ± 12 / 168	166–170	< 0.001	0.12	0.004
Benzo(a)anthracene (4) (BaA) 0.1	223 ± 5 / 222	220–228	251 ± 1 / 251	250–252	231 ± 12 / 231	229–232	< 0.001	0.05	< 0.001
Chrysene (4) (Chry) 0.01	ND	ND	339 ± 12 / 339	337–341	ND	ND	–	–	–
Fluoranthene (4) (Fla) 0.001	267 ± 15 / 266	265–268	270 ± 0.7 / 269	269–270	265 ± 41 / 267	266–270	0.032	0.17	0.002
Pyrene (4) (Pyr) 0.001	279 ± 31 / 279	278–280	278 ± 15 / 278	276–279	274 ± 5 / 272	270–279	0.18	0.1	0.2
Benzo(a)pyrene (5) (BaP) 1	ND	ND	ND	ND	287 ± 47 / 286	283–292	–	–	–
Benzo(b)fluoranthene (5) (BbF) 0.1	ND	ND	301 ± 41 / 301	300–3012	299 ± 15 / 299	298–301	–	–	0.18
Benzo(k)fluoranthene (5) (BkF) 0.1	ND	ND	318 ± 75 / 318	317–318	316 ± 87 / 316	315–317	–	–	0.04
Dibenzo(a,h)anthracene (5) (DBA) 1	41 ± 4 / 41	37–46	9 ± 1 / 9	8–10	54 ± 21 / 54	52–56	< 0.001	0.01	< 0.001
Indeno(1,2,3,c,d)pyrene (6) (IP) 0.1	50 ± 1 / 49	49–51	17 ± 7 / 17	15–19	88 ± 4 / 88	84–92	< 0.001	< 0.001	< 0.001
Benzo (g,h,i)perylene (6) (BghiP) 0.01	22 ± 1 / 22	21–22	5 ± 2 / 5	2.6–8	28 ± 3 / 28	28–29	0.001	< 0.001	< 0.001

TEF for individual PAHs relative to BaP as reported by Nisbet and LaGoy (1992), except TEF values for Cor and BeP which were adopted from Malcom and Dobson (1994); p = probability value, significant when < 0.05; ∑PAHs = sum of non–alkylated total PAHs.

∑COMB = PAHs of combustion origin i.e., BaA, BaP, BbkF, BghiP, Chry, Fla, IP, Pyr (Prahl and Carpenter, 1983).

∑ 7Carcinogenic PAHs = BaA, BaP, BbkF, BghiP, IP, Pyr; LMPAHs = low molecular weight PAHs; HMPAHs = high molecular weight PAHs

SG = Sohdra versus Gujranwala; SW = Sohdra versus Wazirabad; GW = Gujranwala versus Wazirabad.

Table 4. Sum of PAHs concentration (combustion origin and ∑7Carcinogenic PAHs) and diagnostic ration in the atmosphere of sampling sites.

Sites	Sohdra Mean ± S.dev Med	Min–Max	Gujranwala Mean ± S.dev Med	Min–Max	Wazirabad Mean ± S.dev Med	Min–Max	Lahore Mean ± S.dev Med	Min–Max	Rawalpindi Mean ± S.dev Med	Min–Max	Islamabad Mean ± S.dev Med	Min–Max
ΣPAHs	1389 ± 52 / 1391	1375–1398	2397 ± 44 / 2397	2393–2401	2332 ± 164 / 2422	2143–2430	2621 ± 445 / 2862	2108–2894	2359 ± 27 / 2359	2352–2366	1735 ± 17 / 1636	1631–1938
ΣCOMB	841 ± 15 / 839	837–846	1778 ± 55 / 1778	1773–1782	1698 ± 163 / 1787	1511–1797	2026 ± 432 / 2221	1532–2326	1763 ± 43 / 1763	1756–1770	124 ± 93 / 1138	1120–1464
Σ7Carcinogens	574 ± 6 / 574	569–579	1169 ± 43 / 1169	1166–1172	1523 ± 11 / 1523	1511–1532	1549 ± 328 / 1734	1171–1743	1161 ± 47 / 1160	1156–1165	870 ± 13 / 877	855–877
IP/(IP+BghiP)	0.7 ± 0.01 / 0.7	0.6–0.7	0.77 ± 0.1 / 0.76	0.69–0.86	0.76 ± 0.01 / 0.76	0.75–0.77	0.7 ± 0.1 / 0.68	0.68–0.8	0.8 ± 0.03 / 0.82	0.8–0.85	0.68 ± 0.1 / 0.68	0.6–0.68
Fla/(Fla+Pyr)	0.5 ± 0.06 / 0.49	0.4–0.49	0.48 ± 0.1 / 0.49	0.46–0.49	0.33 ± 0.28 / 0.49	0.08–0.49	0.5 ± 0.1 / 0.49	0.47–0.5	0.48 ± 0.1 / 0.49	0.45–0.49	0.83 ± 0.3 / 1	0.5–1
Ant/(Phe+Ant)	0.16 ± 0.01 / 0.11	0.14–0.16	0.11 ± 0.01 / 0.11	0.1–0.12	0.24 ± 0.01 / 0.24	0.23–0.25	0.08 ± 0.07 / 0.1	0.01–0.13	0.04 ± 0.01 / 0.04	0.03–0.05	0.06 ± 0.02 / 0.05	0.05–0.08
BaP/(BaP+Chry)	1 ± 0.05 / 1	1–1.5	0.43 ± 0.1 / 0.43	0.41–0.43	1.1 ± 0.1 / 1.1	1–1.2	0.6 ± 0.1 / 0.5	0.45–0.7	0.4 ± 0.03 / 0.42	0.4–0.42	0.81 ± 0.3 / 1	0.4–1
Fl/(Pyr+Fl)	0.15 ± 0.06 / 0.15	0.12–0.15	0.10 ± 0.04 / 0.10	0.1–0.11	0.19 ± 0.06 / 0.19	0.14–0.2	0.05 ± 0.03 / 0.04	0.03–0.08	0.2 ± 0.07 / 0.2	0.15–0.17	0.69 ± 0.5 / 1	0.06–1
ΣCOMB/ΣPAHs	0.6 ± 0.01 / 0.6	0.5–0.6	0.74 ± 0.1 / 0.74	0.71–0.74	0.73 ± 0.02 / 0.74	0.7–0.74	0.8 ± 0.04 / 0.8	0.7–0.8	0.75 ± 0.1 / 0.75	0.7–0.75	0.71 ± 0.04 / 0.7	0.7–0.76

ΣPAHs = sum of non-alkylated total PAHs.
ΣCOMB = PAHs of combustion origin i.e., BaA, BaP, BbkF, BeP, BghiP, Chry, Fla, IP, Pyr (Prahl and Carpenter, 1983).
Σ7Carcinogenic PAHs = BaA, BaP, BbkF, BghiP, IP, Pyr.

were dominant in both cities, however, in Gujranwala, the contribution of vehicular exhaust and gasoline was more prominent.

The level of PAH-congeners in Wazirabad showed a mixed source of LM-PAHs and HM-PAHs as the comparative data showed that PAH-congeners were high in Wazirabad versus Gujranwala. High concentration of 5-rings PAHs indicated the industrial emission especially from the combustion activities. In general, the profile of PAHs in Wazirabad showed more HM-PAHs emerging from both traffic and combustion-emission. Higher values of Chry and BkF revealed a possible emissions from the coal (Smith and Harrison, 1998; Ravindra *et al.*, 2008) and diesel combustion (Kwon *et al.*, 2008), whereas BghiP also mark gasoline combustion emissions (Kwon *et al.*, 2008 and reference therein). The Fla, Phe, IP, BghiP are markers of fossil-fuel combustion (Kwon *et al.*, 2008). The mobiles sources, especially heavy-duty diesel trucks emit light weight PAHs (Naph, Fla, Pyr) (Marr *et al.*, 1999). Moreover, the HM-PAHs (e.g., BaP, DBA) are usually dominant in the exhaust emission of the light-duty gasoline-powered vehicles (Miguel *et al.*, 1998; Wingfors *et al.*, 2001). In addition to this, the 4- and 5-rings PAHs as reported by Marr *et al.* (1999) are also released in the exhaust emission of the light-duty vehicles, similarly heavy-duty vehicle mostly release 3-rings PAHs.

Both Sohdra and Wazirabad towns are 42 and 36 km away from Gujranwala city (both are a part of District Gujranwala), respectively. A likely explanation of the profile observed in the atmosphere of these cities is that, the Gujranwala is one of the major industrial cities of Pakistan (less the 75 km away from Lahore) which is located close to grand trunk- road (GT-road) of Pakistan (Kamal *et al.*, 2014a, b). In addition to Lahore and Gujranwala cities, the Wazirabad and Sohdra also possess a segment of rural population, where the use of coal/wood and other biomasses is common for cooking purposes. There are many brick kilns located in the vicinity of Gujranwala, Wazirabad and Sohdra, where the wood/coal and a huge amount of cheaper fuel, including scrap rubber/tyre pieces to fire brick kilns. In many other cities of Pakistan, the brick kiln industry together with the presence of large segment of rural population where daily combustion of biomass fuel is common, which releases additional amount of PAHs on daily basis, and the atmospheric PAHs concentration in these areas is further supplemented by the heavy traffic exhaust.

We used the coefficient of divergence analysis (CD) in order to evaluate the divergence of PAH components between different zones, to identify whether the PAHs had the same source of origin and vice versa. According to the Wongphatarakul *et al.* (1998); a CD value < 0.269 reflects a probable divergence between particles in two zones. Considering the proximity of zone-B and zone-C, it was suspected that the source of PAHs in these zones could be similar; however, a value of CD = 0.55 (Table 1) approaching 1, showed that the two zones received PAHs from independent source, which could be high industrial and traffic input in the zone-B and Zone-C respectively.

The concentration of ∑PAHs in the ambient air of three districts (Fig. S1 in supplementary file) was regressed against

the number of brick produced per annum as reported by Tahir *et al.* (2010). The results provided further evidence of wood combustion activities and influence of the brick kiln sectors in three districts. According to the results ~88 percent of the atmospheric PAHs could be attributed to the wood combustions ($R^2 = 0.88$), whereas more than 50 percent of wood combustion could be related to the brick kiln sector ($R^2 = 0.53$).

Source Apportionment of Atmospheric PAHs Using Diagnostic Ratios (DRs)

We used regression scatter plot to indentify the traffic driven (LM-PAHs) PAHs from those generated during the combustion of biomass fuel (mostly HM-PAHs). Figs. S1– S4 shows that there was a strong negative association between the ∑LM-PAHs/HM-PAHs ratios and the ∑COM-PAHs which showed that the large proportion of the PAHs emission in these cities could be associated with biomass mass combustion activity (further confirmed by strong association between ∑PAHs and ∑COMB-PAHs) (see Figures in S1).

The molecular diagnostic ratios (DRs) of PAHs are commonly used as a tool for the identification characterization/ identification of PAHs emission sources (Yunker *et al.*, 2002); in a certain environmental compartments, the profile and composition of PAHs reflects the individual source of emission (Wang *et al.*, 2007). It is known that the concentration different PAHs congeners depend upon the source from which they are originated. The DRs were used in this study was based on the previous knowledge and current concentration of PAHs congeners detected in air. The ratios which are most commonly used were adopted from different literature studies to gain the most relevant qualitative information on PAHs sources (See also Fig. S1 in the supplementary materials S1) (Table 4).

The general profile of PAHs represents that the cities, where low pollution was detected, had a high load of LM-PAHs. The transition point of combustion and petroleum sources of 0.1 is taken for an Ant/(Phe + Ant) ratio is very crucial in determination of sources, i.e., value of < 0.1 indicates and input of patrogenic sources, while a ratio of > 0.1 represent pyrogenic source or, combustion of petroleum, wood/coal, etc. According to our result (Fig. S1; Table 4) city Lahore, Rawalpindi and Islamabad, all had values of this ratio < 0.1 indicating a dominance of petrogenic sources in these cities. The Ant/(Phe + Ant) ratios was > 0.1 in Gujranwala, Sohdra and Wazirabad cities, which represented a dominance of combustion sources possibly in brick kiln unite in the surrounding areas and use of wood/coal for cooking purpose by a large proportion of rural/sub-urban population in the surrounding areas (Fig. S2).

The of Fl/(Fl/Pyr) between 0.4–0.5 represents an input of petroleum combustion (Table 4) stands for the petroleum input, 0.4–0.5 for petroleum combustion (vehicle, crude oil and liquid fossil fuel), while > 0.5 accounts for the combustion of coal/wood and other biomass (Yunker *et al.*, 2002). The results of calculated diagnostic ratios in Sohdra Wazirabad, Rawalpindi, and Lahore city indicate that PAHs originates mainly from the combustion of petroleum

while biomass also contributed to the atmospheric PAHs profile. However, in Wazirabad the ratios was < 0.4, where as in Islamabad was > 0.5 the emission was dominated by pyrogenic and biomass combustion source respectively. BaP/(BaP + Chry), ratio (> 0.35) indicated that except Gujranwala, all the sites were dominated by pyrogenic, source and fossil fuel/biomass combustion. The IP/(IP + BghiP) ratio > 0.2 also indicated pyrogenic and/or combustion of biomass materials source in all the cites. The ratios of ∑COMB/∑PAHs showed dominance of pyrogenic source in all cities.

CONCLUSIONS

The atmospheric concentrations of EPA-priority 16-PAHs in three districts of Punjab province was largely influenced by the anthropogenic activities. Profile of PAH congeners in selected cities showed that the rural and suburban areas were dominated by pyrogenic release of PAHs, while in the urban areas of Pakistan, the road traffic has major contribution to atmospheric PAHs. In general, the concentration of PAHs in the air was dominated by LM-PAHs as compared to those HM-PAHs. Source apportionment clearly indicated that significant proportion of atmospheric PAHs in the studied areas could be attributed to large-scale wood combustion, in particular, in the brick making sectors. Finally, the study has some potential limitations; firstly, the overall sample remained quite small due to the large area span and difficulty in installing PUF-discs in secure (theft-proof) sites. The use of the diagnostic ratios is also less useful in appropriate sources apportionment. Despite these limitations, the study present PAHs in the ambient data of the three main districts of Punjab Pakistan, for the first time, and will helpful in developing mitigation strategies and pollution-control measure in the future.

ACKNOWLEDGEMENTS

LIST OF ABBREVIATIONS

ATSDR: Agency for Toxic Substance and Disease Registry;
IARC: International Agency for Research on Cancer;
MW: Molecular Weight;
PAHs: Polycyclic aromatic hydrocarbons;
U.S. EPA: United States Environmental Protection Agency;
WHO: World Health Organization.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES

Ahmad, M.N., van den Berg, L.J., Shah, H.U., Masood, T., Buker, P., Emberson, L. and Ashmore, M. (2012). Hydrogen Fluoride Damage to Vegetation from Peri-Urban Brick Kilns in Asia: A Growing but Unrecognised Problem? *Environ. Pollut.* 162: 319–324.

Boffeta, P., Jourenkova, N. and Gustavsson, P. (1997). Cancer Risk from Occupational and Environmental Exposure to Polycyclic Aromatic Hydrocarbons. *Cancer Causes Control* 8: 444–472.

Butt, S., Hartmann, I. and Volker, L. (2013). Bioenergy Potential and Consumption in Pakistan. *Biomass Bioenergy* 58: 379–389.

Choi, H. and Spengler, J. (2014). Source Attribution of Personal Exposure to Airborne Polycyclic Aromatic Hydrocarbon Mixture Using Concurrent Personal, Indoor, and Outdoor Measurements. *Environ. Int.* 63: 173–181.

de Andrade, S.J., Cristale, J., Silva, F.S., Julião Zocolo, G. and Marchi, M.R.R. (2010). Contribution of Sugar-Cane Harvesting Season to Atmospheric Contamination by Polycyclic Aromatic Hydrocarbons (Pahs) in Araraquara City, Southeast Brazil. *Atmos. Environ.* 44: 2913–2919.

Harner, T., Shoeib, M., Diamond, M., Stern, G. and Rosenberg, B. (2004). Using Passive Air Samplers to Assess Urban–Rural Trends for Persistent Organic Pollutants. 1. Polychlorinated Biphenyls and Organochlorine Pesticides. *Environ. Sci. Technol.* 38: 4474–4483.

IARC (1983). Polynuclear Aromatic Compounds. Part 1. Chemical, Environmental and Experimental Data. Lyon, International Agency for Research on Cancer, 1983 (IARC Monographson the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 32).

IARC (1987). Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs, International Agency for Research on Cancer (Volume 1–42). Lyon, France.

Jia, Y., Stone, D., Wang, W., Schrlau, J., Tao, S. and Massey, S.S.L. (2011). Estimated Reduction in Cancer Risk due to PAH Exposures If Source Control Measures during the 2008 Beijing Olympics Were Sustained. *Environ. Health Perspect.* 119: 815–820, doi: 10.1289/ehp.1003100.

Kamal, A., Ali, U., Ramey, M.I., Younas, S.M.Z., Sumbul, S., Malik, R.N. and Rashid, A. (2013). Principle Component Analysis of Flue Gas Exhaust from a Functional Incinerator in The vicinity of Rawalpindi, Pakistan. *Arabian J. Chem.*, in Press. doi: 10.1016/j.arabjc.2013.08.006.

Kamal, A., Qamar, K., Gulfraz, M., Anwar, M.A. and Malik, R.N. (2014a). PAH Exposure and Oxidative Stress Indicators of Human Cohorts Exposed to Traffic Pollution in Lahore City (Pakistan). *Chemosphere* 120: 59–67, doi: 10.1016/j.chemosphere.2014.05.021.

Kamal, A., Malik, R.N., Martellini, T. and Cincinelli, A. (2014b). Cancer Risk Evaluation of Brick Kiln Workers Exposed to Dust Bound PAHs in Punjab Province, Pakistan. *Sci. Total Environ.* 493: 562–570.

Kamal, A., Cincinelli, A., Martellini, T. and Malik, R.N. (2015a). A Review of Pah Exposure from the Combustion

of Biomass Fuel and Their Less Surveyed Effect on the Blood Parameters. *Environ. Sci. Pollut. Res. Int.* 22: 4076–4098, doi: 10.1007/s11356-014-3748-0.

Kamal, A., Cincinelli, A., Martellini, T., Palchetti, I., Bettazzi, F. and Malik, R.N. (2015b). Health and Carcinogenic Risk Evaluation for Cohorts Exposed to PAHs in Petrochemical Workplaces in Rawalpindi City (Pakistan). *Int. J. Environ. Health Res.* 26: 37–57, doi: 10.1080/09603123.2015.1007843.

Kwon, H.O. and Choi, S.D. (2008). Polycyclic Aromatic Hydrocarbons (PAHs) in Soils from a Multi-industrial City, South Korea. *Sci. Total Environ.* 470–471: 1494–1501.

Li, W., Wang, C., Wang, H., Chen, J., Shen, H., Shen, G., Huang, Y., Wang, R., Wang, B., Zhang, Y., Chen, H., Chen, Y., Su, S., Lin, N., Tang, J., Li, Q., Wang, X., Liu, J. and Tao, S. (2014). Atmospheric Polycyclic Aromatic Hydrocarbons in Rural and Urban Areas of Northern China. *Environ. Pollut.* 192: 83–90.

Lohmann, R., Harner, T., Thomas, G.O. and Jones, K.C. (2000). A Comparative Study of the Gas-particle Partitioning of PCDD/Fs, PCBs, and PAHs. *Environ. Sci. Technol.* 34: 4943–4951.

Ma, W.L., Li, Y.F., Qi, H., Sun, D.Z., Liu, L.Y. and Wang, D.G. (2010). Seasonal Variations of Sources of Polycyclic Aromatic Hydrocarbons (PAHs) to a Northeastern Urban City, China. *Chemosphere* 79: 441–447.

Malcom, H.M. and Dobson, S. (1994). The Calculation of an Environmental Assessment Level (EAL) for Atmospheric PAHs Using Relative Potencies. Department of the Environment: London, UK.

Marr, L.C., Kirchstetter, T.W., Harley, R.A., Miguel, A.H. and Hering, S.V. (1999). Characterization of Polycyclic Aromatic Hydrocarbons in Motor Vehicles Fuels and Exhaust Emissions. *Environ. Sci. Technol.* 33: 3091–3099.

Masiol, M., Hofer, A., Stefania, S., Rossano, P., Giancarlo, R. and Bruno, P. (2012). Carcinogenic and mutagenic Risk Associated to Airborne Particle-phase Polycyclic Aromatic Hydrocarbons: A Source Apportionment. *Atmos. Environ.* 60: 375–382.

Meiners, R.E. and Yandle, B. (1995). Rowman & Littlefield Publishers, Taking the Environment Seriously. Inc. USA. 3 Henrietta Street, London WC2E 8LU, England.

Miguel, A.H., Kirchstetter, T.W., Harley, R.B. and Hering, R.A. (1998). On-road Emissions of Particulate Polycyclic Aromatic Hydrocarbons and Black Carbon from Gasoline and Diesel Vehicles. *Environ. Sci. Technol.* 32: 450–455.

Nam, J.J., Song, B.H., Eom, K.C., Lee, S.H. and Smith, A. (2003). Distribution of Polycyclic Aromatic Hydrocarbons in Agricultural Soils in South Korea. *Chemosphere* 50: 1281–1289.

Nisbet, C. and Lagoy P. (1992). Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). *Regul. Toxicol. Pharm.* 16: 290–300.

OEHHA (1993). Benzo[a]pyrene as a Toxic Air Contaminant. Part B. Health Effects of Benzo[a]pyrene. Berkeley, CA: California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section.

OEHHA (2003). The Air Toxics Hot Spots Program Guidance Manual for Preparation of Health Risk Assessments. Oakland, CA: California Environmental Protection Agency, Office of Environmental Health Hazard Assessment.

OEHHA (2005). Air Toxics Hot Spots Program Risk Assessment Guidelines. Oakland, CA: California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section.

Prahl, F.G. and Carpenter, R. (1983). Polycyclic Aromatic Hydrocarbon (PAH) -Phase Associations in Washington Coastal Sediment. *Geochim. Cosmochim. Acta* 47: 1013–1023.

Ravindra, K., Bencs, L., Wauters, E., Hoog, J., Deutsch, F., Roekens, E., Bleux, N., Berghmans, P. and Grieken, R. (2006). Seasonal and Site-specific Variation in Vapour and Aerosol Phase PAHs over Flanders (Belgium) and their Relation with Anthropogenic Activities. *Atmos. Environ.* 40: 771–785.

Ravindra, K., Sokhi, R. and Van Grieken, R. (2008). Atmospheric Polycyclic Aromatic Hydrocarbons: Source Attribution, Emission Factors and Regulation. *Atmos. Environ.* 42: 2895–2921.

San Jose, R., Perez, J.L., Callen, M.S., Lopez, J.M. and Mastral, A. (2013). Bap (PAH) Air Quality Modelling Exercise over Zaragoza (Spain) Using an Adapted Version of WRF-CMAQ Model. *Environ. Pollut.* 183: 151–158, do: 10.1016/j.envpol.2013.02.025.

Shi, Z., Tao, S., Pan, B., Fan, W., He, X.C., Zuo, Q., Wu, S.P., Li, B.G., Cao, J., Liu, W.X., Xu, F.L., Wang, X.J., Shen, W.R. and Wong, P.K. (2005). Contamination of Rivers in Tianjin, China by Polycyclic Aromatic Hydrocarbons. *Environ. Pollut.* 134:97–111.

Simcik, M.F., Franz, T.P., Zhang, H. and Eisenreich, S.J. (1998). Gas-Particle partitioning of PCBs and PAHs in the Chicago Urban and Adjacent Coastal Atmosphere: States of Equilibrium. *Environ. Sci. Technol.* 32: 251–257.

Smith, D.J.T., Edelhauser, E.C. and Harrison, R.M. (1995). Polycyclic Aromatic Hydrocarbon Concentrations in Road Dust and Soil Samples Collected in the United Kingdom and Pakistan. *Environ. Technol.* 16: 45–53.

Smith, D.J.T. and Harrison, R.M. (1998). Polycyclic Aromatic Hydrocarbons in Atmospheric Particles. In *Atmospheric Particles*, Harrison, R.M. and Van Grieken, R. (Eds.), Wiley.

Stone, E., Schauer, J., Quraishi, T.A. and Mahmood, A. (2010). Chemical Characterization and Source Apportionment of Fine and Coarse Particulate Matter in Lahore, Pakistan. *Atmos. Environ.* 44: 1062–1070.

Tahir, S.N.A., Rafique, M. and Alaamer, A.S. (2010). Biomass Fuel Burning and its Implications: Deforestation and Green House Gases Emissions in Pakistan. *Environ. Pollut.* 158: 2490–2495.

Taioli, E., Sram, R.J., Binkova, B., Kalina, I., Popov, T.A., Garte, S. and Farmer, P.B. (2007). Biomarkers of Exposure to Carcinogenic PAHs and their Relationship with Environmental Factors. *Mutat. Res.* 620: 16–21.

U.S. EPA (1989). United States Environmental Protection Agency. Risk Assessment Guidance for Superfund. Human Health Evaluation Manual. EPA/540/1-89/002, Vol. I. Washington, DC: Office of Soild Waste and Emergency Response; 1989.

U.S. EPA (2005). United States Environmental Protection Agency. Guidelines for Carcinogen Risk Assessment. Washington DC: Risk Assessment Forum [EPA/630/P-03/001F].

U.S. EPA (2009). United States Environmental Protection Agency. Risk Assessment Guidance for Superfund. Vol. I: Human Health Evaluation Manual., F, Supplemental Guidance for Inhalation Risk Assessment. EPA/540/R/070/002, Office of Superfund Remediation and Technology Innovation, Washington, DC, 2009. http://www.epa.gov/oswer/riskassessment/ragsf/pdf/part f_2009 01_final.pdf accessed 12-1-2013.

U.S. EPA (2010). United States Environmental Protection Agency. Development of a Relative Potency Factor (RPF) Approach for Polycyclic Aromatic Hydrocarbon (PAH) Mixtures. External review draft. Washington, DC: U.S. EPA, Integrated Risk Information System.

UNEC (United Nations Economic Commission for Europe) (1998). Aarhus Protocol on Persistant Organic Pollutants, http: //live.unece.org/env/lrtap/pops h1.html.

von Schneidemesser, E., Stone, E.A., Quraishi, T.A., Shafer, M.M. and Schauer, J.J. (2010). Toxic Metals in the Atmosphere in Lahore, Pakistan. *Sci. Total Environ.* 408: 1640–1648.

Wang, Z., Chen, J.W., Qiao, X.L., Yang, P., Tian, F.L. and Huang, L.P. (2007). Distribution and Sources of Polycyclic Aromatic Hydrocarbons from Urban to Rural Soils: A Case Study in Dalian, China. *Chemosphere* 68: 965–971.

WHO (World Health Organization) (2000). Air Quality Guidelines for Europe. 2nd ed. Copenhagen: WHO, Regional Office for Europe.

WHO/IPCS (1998). Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons. Environmental Health Criteria 202. Geneva, Swiss.

Wingfors, H., Sjodin, A., Halgund, P. and Brorstrom-Lunden, E. (2001). Characterization and Determination of Profiles of Polycyclic Aromatic Hydrocarbons in a Traffic Tunnel in Gothenburg, Sweden. *Atmos. Environ.* 35: 6361–6369.

Wongphatarakul, V., Friedlander, S.K. and Pinto, J.P. (1998). A Comparative Study of $PM_{2.5}$ Ambient Aerosol Chemical Databases. *Environ. Sci. Technol.* 32: 3926–3934.

Wu, D., Wang, Z., Chen, J., Kong, S., Fu, X., Deng, H., Shao, G. and Wu, G. (2014). Polycyclic Aromatic Hydrocarbons (PAHs) in Atmospheric $PM_{2.5}$ and PM_{10} at a Coal-Based Industrial City: Implication for PAH Control at Industrial Agglomeration Regions, China. *Atmos. Res.* 149: 217–229.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchelld, R.H., Goyette, D.Y. and Sylvestre, S. (2002). PAHs in the Fraser River Basin: A Critical Appraisal of PAH Ratios as Indicators of PAH Source and Composition. *Org. Geochem.* 33: 489–515.

Zhang, Y. and Tao, S. (2009). Global Atmospheric Emission Inventory of Polycyclic Aromatic Hydrocarbons (PAHs) for 2004. *Atmos. Environ.* 43: 812–819.