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Distribution, toxicity level, and concentration of polycyclic aromatic hydrocarbons (PAHs) in surface soil and groundwater of Rawalpindi, Pakistan

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ABSTRACT

In this study, the distribution, toxicity level, and relationship of polycyclic aromatic hydrocarbons (PAHs) with total organic content (TOC) have been investigated using surface soil and ground water samples from an area adjacent to petrochemical plant in Pakistan. Six PAHs, naphthalene, acenaphthene, phenanthrene, anthracene, flouranthene, and chrysene, were selected from the 16 Environment Protection Agency priority pollutants list. Σ PAHs range from 2,700 to 4,443 µg/g (average: 3,672 ± 592 µg/g) in soil and 201–1,634 ng/L (average: 763 ± 377 ng/L) in water. The compositional profile of PAHs revealed that low molecular weight 3–4 ring PAHs were predominant. The ratios of phenanthrene/anthracene reflected the pyrogenic origin of PAHs. The relationship of PAHs with TOC has also been investigated and a positive correlation was observed between Σ PAHs and TOC. This indicates that partitioned in organic matter may be the possible source of PAHs in water. An assessment using widely cited guidelines indicates that water samples do not pose biological impact, while soil can pose a threat of lung cancer.

Keywords: PAHs; Carcinogenic; Toxic equivalency factor; Gas chromatograph; Total organic content

1. Introduction

Groundwater contamination with pollutants poses a serious threat to human well-being due to the fact that it is widely used for drinking and irrigation. Surface soil contamination acts as a permanent source of ground water pollution. Toxic pollutants like polycyclic aromatic hydrocarbons (PAHs) are the major culprits in urban areas and can pose risk of lung cancer [1]. A study by Zhang et al. [2] and Goldman et al. [3] also proved increased susceptibility to lung cancer among urban inhabitants exposed to PAHs, as compared to rural inhabitants and smokers. PAHs are ubiquitous organic compounds and their alkylated homologous. The possible mobile sources are incomplete combustion or pyrolysis of organic material [4] vehicular emissions, tire wear debris, asphalt particles [5], and stationary combustion sources or crematoria [5]. Sources of PAHs in urban atmosphere include automobiles, resuspended soils, refineries, and power plants [6–8]. PAHs are also present in sedimentary rocks and petroleum [9,10].

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PAHs in groundwater may originate from polluted surface water bodies, agricultural irrigation with effluents, and leachates from solid waste disposal sites or contaminated soil. Groundwater is naturally filtered as it flows through various soil matrices, and PAHs adsorb well into organics. PAHs are produced in great quantities in chemical manufacturing, petroleum refining, and metallurgical processes. These compounds have been detected in the atmosphere, water, soil, sediments, and food [11]. Atmospheric deposition has been regarded as a main pathway for the loading of PAHs to water bodies [12]. Distribution of PAHs in different phases of the environment depends on their physical/chemical properties, such as molecular weight, solubility, vapor pressure, and sorption coefficients [13]. Owing to their low solubility and high hydrophobicity, they remain associated with particulate matter and deposit in surface soils and sediments [14]. Hence, the occurrence of PAHs in groundwater and soil by these processes is an important problem because PAHs can be hazardous in low concentrations and some PAHs degrade relatively slowly [15]. At present, there is growing concern about the need for the evaluation of the extent of groundwater contamination and the only remedy is extensive pumping. It has also been reported that disinfection of drinking water may lead to oxygenated and chlorinated PAHs, i.e. compounds more toxic than the parent PAHs [16]. In Pakistan, there is no national monitoring program concerning the determination and identification of organic pollutants and few studies have been carried to measure trace organic compounds in groundwater [17,18]. In addition, there is no data available regarding the concentration and toxicity level of PAHs in drinking water soil or air. Therefore, the objective of this research is the determination and quantification of the exposure level of PAHs in surface soil and groundwater in Pakistan.

2. Materials and methods

2.1. Sample collection and preparation

Rawalpindi is a densely populated city of Pakistan with heavy traffic load and industrial activity within the city. One of the largest, working petroleum refining units has been situated at Kotha Kalan village for more than 80 years. To evaluate the effect of the petrochemical industry on the surface soil and groundwater of the adjacent area, sampling was done within 1 km radius of the eastern side of the industry from the village Kotha Kalan (population 10,000), about 3 km upstream from Sawan River. For water sampling, 44 water samples (S1–S44) from boreholes (depth ranges 30–60 m) were collected twice. One water sample (S45) was collected from the university campus (tubewell) as a control. Water samples were collected according to American Public Health Association [19] in 500 ml glass bottles (amber color to prevent light) previously cleaned with phosphate-free detergent and presoaked in 10% sulfuric acid for 24 h rinsed with tap water deionized (DI) water and finally rinsed three times with n-hexane. Samples were transported in iceboxes after taking field data of pH, electrical conductivity, and total dissolved solids (TDS) liquid–liquid extraction and following this the clean-up was done [20].

Soil sampling was done in nine sampling sites (S1– S9) from Kotha Kalan village and one from the university campus about 30 km away from the suspected contamination source. Surface soil samples were collected with auger after removing the top layer (1 cm) with a spatula. The samples were transported in jars previously cleaned as described. The analysis was carried out according to the USEPA method [21]. Soil samples were dried in air, homogenized, and passed through a 1 mm stainless steel sieve.

2.2. Chemical reagents

PAHs standards naphthalene (Nap), acenaphthene (Ace), phenanthrene (Phe), anthracene (Ant), flouranthene (Flu), and chrysene (Chr) were purchased from Chiron chemicals, Australia. Silica gel (80–100 mesh), anhydrous sodium sulfate, and high pressure liquid chromatography grade n-hexane to process samples and analysis were purchased from Merck Germany. DI water was produced by Milli-Q-system (Millipore Co. USA).

2.3. Determination of total organic content

Soil and water total organic content (TOC) were analyzed using a TOC analyzer (Analytic Jena) and for water content analyses, the weight loss method was used as described in [22].

2.4. Chromatographic analysis

A Shimadzu 2010 gas chromatograph (GC) equipped with a flame ionization detector was used for identification of PAHs, equipped with TRB five capillary column $(30 \text{ m} \times 0.32 \text{ mm} \text{ and } 0.5 \mu \text{m} \text{ film}$ thickness). The injections were made in a split mode of 1:50 with a delay time of 4 min and kept at 280°C: The GC oven was held at 100°C for 2 min and programed to rise to 280°C at a rate of 10°C/min for

24 min. The carrier gas was helium at a flow rate of $1.0 \,\text{mL/min}$.

2.5. Quality assurance

A quality control program was carried out, which included the following: preextraction of thimbles and silica with solvent. A blank was run with each set of analysis. Quantification of PAHs was carried out using external standards with a coefficient of calibration curves higher than 0.986. A known amount of PAH standard was added to three blank samples of water and soil and extracted using the method used for analysis of soil and water samples to check recovered concentrations it ranged from 68 to 92%.

2.6. Extraction and analysis

All soil analytes were quantified through Soxhlet extract of each soil sample. Ten grams were extracted using the Soxhlet extractor (Gerhardt EV-16) with 200 ml of n-hexane solvent for 24 h as Soxhlet extraction gives double extraction efficiency as compared to the direct ultrasonic technique [23]. The extract was concentrated to 5 ml using rotary evaporator [20]. For water samples, the extraction was carried out using the liquid-liquid extraction method [24]. The apparatus for this method consisted of a 50 ml volume separating funnel mounted on a retort stand. The separating funnel was thoroughly washed and dried over night in a muffle furnace at an elevated temperature. Prior to use, the funnel was rinsed vigorously with n-hexane for several minutes. This was removed and allowed to drain and dry completely in a fume cupboard. Water sample (10 ml) to be extracted was transferred to the separating funnel and to this was added 10 ml of n-hexane. This was shaken vigorously for 2 min and allowed to separate and settle. After 10 min, the organic layer was removed and the process repeated with the aqueous layer twice. The three portions of the organic phase were combined and evaporated to 1 ml volume using a rotary evaporator. One micro liter of each sample extract was injected into GC. An internal calibration curve, with five levels of concentration of each PAH was used to set the response factor of each analyte.

3. Results and discussions

3.1. Levels of PAHs in surface soils

PAHs detected in top soil samples were present in relatively high concentrations. In the present study, top soil has shown a wider spectrum and higher concentrations of PAHs. Similar findings were reported by Li et al. [25], who indicated that most PAHs would be restricted to top soil. Σ PAHs concentration in soil is presented in Table 1 and Σ PAHs ranges between 2,700 and 4,443 μ g/g (average: 3,672 ± 592 μ g/g). Nap is below detection limits in 80% of the samples because of its high volatility. Phe and Ant are among the highest found concentrations of PAHs (Fig. 1). The highest average concentration of PAHs in agricultural soil samples S1, S2, and S3 is 4,028, 4,387, and $3,861 \,\mu g/g$, respectively. Agriculture soils were taken from fallow land before sowing of the next season and PAHs attributed to surface deposition. Maximum concentration of PAHs in an open place is understandable since they are considered to be multihop chemicals. The term multihop is used for specific partitioning properties of persistent organic pollutants and for low molecular weight (LMW) compounds.

Table 1						
Concentrations of PAHs.	TOC	contents.	and	molecular	indices	of

	Description of location	Σ PAHs (µg/g)	TOC (mg/L)	Molecular indices	
				Phe/Ant	Ant/(Ant+Phe)
S1	Agricultural soil + fellow land	4,028	70	1.81	0.36
S2	Agricultural soil + fellow land	4,387	80	1.56	0.39
S3	Agricultural soil + fellow land	3,861	65	1.10	0.48
S4	Residential soil	3,863	75	1.47	0.40
S5	Residential soil	3,369	68	9.84	0.09
S6	Residential + roadside soil	4,443	211	6.11	0.14
S7	Commercial soil	3,109	124	1.08	0.48
S8	Commercial soil	3,290	159	1.43	0.41
S9	Commercial soil	2,700	79	4.59	0.18
S10	Control soil	877	50	0.57	0.64

PAHs in soil



Fig. 1. Level of PAHs in soil samples.

LMW compounds have a tendency for long-range transport and get deposited on surfaces through air–surface exchange. Repeated cycles of deposition and evaporation often driven by seasonal or diurnal temperature changes allow the gradual transfer of these compounds over long distance [26–28].

In sample S6, the highest average PAHs concentration was observed. The site was on the roadside and surrounded by tall buildings, so emitted particulate associated PAHs might not have got the chance to disperse, thus settling in the immediate vicinity. Frequent change of gear and slow speed traffic in residential areas also results in the highest PAH emissions [29]. The lowest concentration was observed in S9 sample, a commercial site near a playground where green grass cover adsorbs maximum PAHs. The control sample S10 was collected from unused land in the university campus. Only a few guidelines are available worldwide for concentrations of PAHS in soil. Therefore, PAHs concentrations were compared with Polish standards $(0.2-10 \mu g/g)$ and Dutch standards $(0.025-0.05 \,\mu g/g)$ [30]. The comparison suggested that total PAHs concentration in soil exceeds the Polish standards. The effects range low value guidelines established by Long et al. [31] suggest a 16 ng/g cut-off for Ace however, all soil samples exceed this cut-off line. This suggests a harmful effect on soil biota.

3.2. Level of PAHs in water dissolved phase

The concentrations of PAHs in groundwater from Kotha Kalan at different sampling sites are presented in Fig. 2. From this it can be seen that Ace and Phe were present in the majority of water samples. The level of Σ PAHs fluctuated from 201 (S16) to 1,634 ng/L (S45) with the mean value of 763 ng/L. Compared with Agra groundwater 13.27–64.29 ng/L [32] and Ismailia Egypt 8 µg/L [33], the results indicated that the level of PAHs in water is mid-line. Concentrations



Fig. 2. Level of PAHs in water dissolved phase in water samples.

of PAHs exceeding $10 \,\mu\text{g/L}$ can suggest that the water is heavily contaminated by PAHs [34]. However, lethal concentration (L50) less than $10 \,\mu\text{g/L}$ has been reported for various organisms [35].

The obtained results also indicate that the total level of selected PAHs in all water samples have no harmful biological effects. The physiochemical properties of compounds can predict environmental fate and the behavior of hydrophobic compounds. A linear relationship is observed between the values of TOC and Σ PAHs (Tables 2(a) and 2(b)). The PAHs and

Table 2a

Concentrations of PAHs, TOC contents, and molecular indices of PAHs in water

Samples	ΣPAHs	TOC	Molecular indices			
	(ng/L)	(mg/L)	Phe/Ant	Ant/ (Ant + Phe)		
S1	1,156	11.6	0.55	0.65		
S2	1,469	13.66	3.81	0.21		
S3	1,118	9.01	7.55	0.12		
S4	1,161	29.34	7.95	0.11		
S5	529.9	24.31	0.37	0.73		
S6	330	20.67	0.22	0.82		
S7	846	16.9	0.49	0.67		
S8	281	14.99	4.59	0.18		
S9	489	15.48	7.59	0.12		
S10	559	14.48	2.78	0.26		
S11	822	5.00	0.41	0.71		
S12	993	11.59	1.87	0.35		
S13	865	2.00	_	_		
S14	388	5.00	0.61	0.62		
S15	726	1.08	0.93	0.52		
S16	201	1.99	_	1.00		
S17	1,209	6.60	0.91	0.52		
S18	500	2.00	1.25	0.44		
S19	856	4.9	0.18	0.85		
S20	854	4.24	2.40	0.29		
S21	1,069	1.49	1.13	0.47		
S22	517	1.10	0.68	0.60		
S23	639	2.08	1.07	0.48		

Table 2b Concentrations of PAHs, TOC contents, and molecular indices of PAHs in water

Samples	ΣPAHs	TOC	Molecular indices		
	(ng/L)	(mg/L)	Phe/Ant	Ant/ (Ant + Phe)	
S24	158	3.6	3.44	0.23	
S25	1,370	6.67	0.98	0.50	
S26	1,552	5.42	0.15	0.87	
S27	979	4.08	0.29	0.78	
S28	868	3.23	2.20	0.31	
S29	347	1.35	0.47	0.68	
S30	377	3.51	0.47	0.68	
S31	415	2.32	0.43	0.70	
S32	376	4.48	_	1.00	
S33	394	4.23	0.98	0.50	
S34	672	4.73	1.26	0.44	
S35	1,244	8.57	1.14	0.47	
S36	449	6.48	1.43	0.41	
S37	815	4.12	2.62	0.28	
S38	380	1.13	0.48	0.68	
S39	1,040	1.46	0.59	0.63	
S40	316	4.16	0.63	0.61	
S41	522	2.81	0.56	0.64	
S42	1,107	3.83	0.24	0.81	
S43	839	6.28	0.19	0.84	
S45	1,634	2.00	0.53	0.65	
S46 (control)	1,125	3.08	0.29	0.77	

TOC show variable behavior, the possible reason for this may be the values of TOC and PAHs come from different sources and low values of TOC show that the inorganic matrix besides organic matrix affects sorption of PAHs [36]. LMW PAHs (3–4 rings) predominates in water, it could be explained that relatively low vapor pressure and water solubility of these PAHs can be the major reason [37]. Among individual PAHs, Chr shows consistent behavior, while Ace, Phe, and Ant represent fairly fluctuating behavior in water samples.

3.3. PAHs profile

The composition pattern of PAHs in water and soil samples is presented in Fig. 3. The Ant; Phe; and Flu contribute 61, 5, and 4.6%, respectively, in water and 29, 57.8, and 4%, respectively, in soil. The presence of LMW PAHs suggests their association with organic content, thus reducing loses by volatilization. In water samples, Ant and Chr were dominant and in soil, Phe and Ant were dominant,



Fig. 3. Composition profile of PAHs in water and soil samples.

contributing >80% of Σ PAHs. The profile indicates that three ring PAHs have maximum adsorption for soil as observed by Saba and Rafique [38]. The higher percentage of Chr (22%) in water than in soil (1.9%) shows its association with TDS in water. Three to four ring PAHs exist in vapor and particulate phases [26,27], so sedimentation from the atmosphere, slow degradation of these compounds, and strong adsorption in soil contributes to the observed pattern of PAHs.

3.4. Toxicity assessment

Occupational exposure limit has not been established for Σ PAHs because of their chemical composition complexity. However, to calculate the risk of carcinogenic PAHs intake an equation factor has been established for PAHs to quantify toxicity potential. B(a)P benzo (a) pyrene-equivalent concentration (BaPeq) is used to estimate toxicity potential. B(a)P is a pentacyclic $(C_{20}H_{12})$ compound, which is mutagenic for human cells in culture [39] and carcinogenic in animal assays [40]. According to Bostrom et al. [41], the toxic equivalent factor (TEF) for B(a)P is (1), which is highest among all PAHs. In the present work, TEFs given by Tsai et al. [42] were employed. B(a)P equivalents were calculated by multiplying mean concentration with corresponding TEF values. The above method is easy to apply; however, it may underestimate risk because limited compounds are considered [43]. TEFs adopted for calculations are 0.001 for Nap, Ace, Phe, and Flu and 0.01 for Ant and Chr. Carcinogenic exposure equivalent for water ranges from 0.03 (Nap) to 2.00 ng/L (Ant) with Σ PAHs of 3.2 ng/L and in soil, it ranges from 0.04 (Nap) to 9.9 (Ant) with Σ PAHs of 12.8 µg/L (Table 3). PAHs toxicity level in soil is 400 times higher than in water and approximately, 14 times higher than roadside soil of Shanghai China $(0.892 \,\mu g \, BaPeq/g)$ [44].

Compound	TEF	Water samples			Soil samples		
		Mean (ng/L)	SD	BaPeq (ng/L)	Mean (µg/L)	SD	BaPeq (µg/L)
Nap	0.001	28.69	59.88	0.03	37.4	61	0.04
Ace	0.001	148.78	216.67	0.15	200.8	80.9	0.20
Phe	0.001	179.24	183.51	0.18	1,963.1	816.3	1.96
Ant	0.01	195.69	167.95	2.00	989.7	535.6	9.90
Flua	0.01	168.53	109.54	0.17	137.2	90.8	0.14
Chr	0.001	71.29	31.86	0.71	64.5	16.3	0.65
ΣPAHs		763.53	377	3.24	3,392	1,045	12.88

Table 3 Average PAHs and BaPeq concentrations

3.5. Correlation of PAHs with TOC

The environmental fate and behavior of volatile organic compounds is ultimately determined by the physico-chemical properties of each compound's organic content, partition coefficient, and salinity [45]. In the present study, the wide disparity in the concentrations of **SPAHs** among water samples was also reflected in the TOC content. When TOC is arranged with increasing order, a very weak or no relationship is found between Σ PAHs and TOC R^2 0.006 for Σ PAHs and TOC as represented in Fig. 4. Soil samples also show a positive relationship of Σ PAHs with TOC (R^2 0.1374) and to some extent a similar distribution pattern (Fig. 5). The highest PAHs contained in soil (S6) $4,443\,\mu g/g$ shows high TOC $112\,m g/L$ According to Wilcke and Amelung [46], only gaseous PAHs may be partitioned directly from the atmosphere to soil organic matter. Overtime they may get deposited in soil. They found a strong correlation between soil organic carbon and more volatile, (i.e. LMW PAHs). Nam et al. [47] also reported good positive correlation between PAHs and TOC (strongest with three-ring PAHs) in Norwegian soil having no prominent anthropogenic source in the vicinity.

3.6. Sources of PAHs

PAHs enter the environment through natural processes or are generated through combustion mechanisms. In order to determine the origin of PAHs, the type and concentration of PAHs should be known. The petroleum derived assemblage contains high amounts of LMW PAHs like Nap, acenaphthalene, and fluorine [48]. Combustion derived PAHs result from pyrolytic synthesis at high temperatures and contain Phe, fluoranthene, pyrene, B(a)P, etc. In the present study, Phe and fluoranthene concentrations 179 ± 183 and 168 ± 109 (ng/L) in water and 1963 ± 816 and $137 \pm 90 \ (\mu g/g)$ in soil, respectively, were found. These results indicate a pyrogenic origin of PAHs as combustion products. The values of phenanthrene/ anthracene (Phe/Ant) and Ant/(Ant+Phe) are extensively used to distinguish the petrogenic and pyrogenic origin of PAHs. Values of Phe/Ant>10 and Ant/(Ant+Phe<0.1) indicate petroleum origin and



Fig. 4. Correlation of Σ PAHs and TOC in water samples.



Fig. 5. Correlation of Σ PAHs and TOC in soil samples.

vice versa indicates the dominance of combustion origin [49–52]. The Phe/Ant values ranges between 1.08 and 9.84 for soil and 0.15 and 7.95 in water, while Ant/(Ant+Phe) ratios range between 0.09 and 0.64 in soil and 0.12 and 1.00 in water (Tables 1, 2(a), and 2 (b)). These values clearly affirmed predominant pyrogenic origin. The results of molecular indices represent that combustion products of PAHs from gas flaring, atmospheric emissions, and vehicular exhaust are the sources of PAHs and atmospheric fall, runoff, and leaching to groundwater are the major pathways of PAHs. There is the possibility of petrogenic contributions also, but the dilution factor is very high which reflects the fact that the environmental self-purification system is working quiet efficiently.

4. Conclusion

The above study concludes that concentrations of PAHs in soil pose a threat to living biota, while in water the selected PAHs do not pose a risk. The investigation of PAHs from groundwater and soil revealed that highest concentration of **SPAHs** in ground water was 1634 ng/L which was significantly higher than the WHO [53] guidelines for PAHs of 10 ng/L. In soil, the highest concentration was $4,443 \,\mu g/g$ which was also very high when compared with Dutch soil standards of $0.02-0.05 \,\mu g/g$ and Polish standards of $0.2-10 \,\mu\text{g/g}$. The selected PAHs showed weak correlation with total organic matter, as organic matter is not the only source of PAHs molecular indices that predicted a pyrogenic origin of PAHs. In addition, high PAHs in agricultural soil revealed the possibility of bioconcentration in crops which should be investigated.

Water sampling points





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