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## Occurrence of polycyclic aromatic hydrocarbons in the Soan River, Pakistan: Insights into distribution, composition, sources and ecological risk assessment<sup>☆</sup>



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### ABSTRACT

Present study investigates the occurrence, distribution and sources of  $\Sigma_{17}$  polycyclic aromatic hydrocarbons (PAHs) in the surface water of Soan River, Pakistan. The concentrations of total PAHs ranged from 61 to 207 ng/l. Low molecular weight (LMW) PAHs were recorded higher in concentrations (64.7 percent) as compared to high molecular weight (HMW) PAHs (35.6 percent). Principal component analysis (PCA) revealed domestic and industrial wastewater discharge, vehicular exhaust, petroleum residues and biomass combustion as the main sources for PAHs contamination. Using the USEPA toxic equivalency factor (TEF) approach: Benzo(a)Pyrene and Dibenzo(a,h)Anthracene contributed highly carcinogenic exposure equivalent. The surface water of the Soan River is found to be slightly polluted with PAHs thereby posing health risks to aquatic bodies.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are important group of organic compounds. They have compressed structures consisting of two or more aromatic rings and have variable physicochemical properties (Jan et al., 2013). Due to their carcinogenicity and toxicity potential to both aquatic and terrestrial organisms, USEPA (1984) listed them as priority pollutants. Taioli et al. (2007) reported the clear evidence of DNA damage and the genotoxic effects related with exposure to PAHs. Exposure to air, water, fish and other food items contaminated with PAHs leads to negative impacts on human health (Martellini et al., 2012).

PAHs find their way into the environment through natural (volcanoes, forest and prairie fires) and anthropogenic sources.

Anthropogenic sources include automotive exhausts, tire degradation, industrial emissions from catalytic cracking, air blowing of asphalt, domestic heating emissions from coal, oil, gas, and wood, refuse incineration, and biomass burning (Baek et al., 1991). PAHs may enter surface water mainly via atmospheric fallout (precipitation, dry deposition), urban runoff, municipal and industrial effluents, and oil spillage or leakage (Katayama et al., 2010). It has been estimated that 10–80 percent of PAHs contribution to the oceans is from atmospheric sources (Moore and Ramamoorthy, 1984). It is estimated that the atmospheric PAH deposition in the waterbodies of Hangzhou city was 530 t/y while surface runoff contributed 30.7 t/y (Chen et al., 2004). After entering the aquatic environment, due to their consequence of hydrophobic nature, PAHs rapidly tend to bound to the particulate matter and eventually end up in the sediments (Qiu et al., 2009).

In Pakistan, there is limitation of studies reported on the surface water pollution for organic contaminants including PAHs. There is lack of baseline data for PAHs pollution in surface water. Only surface water of Chenab River has been assessed to determine its occurrence. The ecology of the Soan River has also been affected due to its proximity to densely inhabited areas and to the

<sup>☆</sup>**Capsule:** Findings indicate low ecosystem risk by Polyaromatic Hydrocarbons in surface waters of the Soan River.

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anthropogenic activities along the river. Moreover, heavy density vehicular emissions in atmosphere and their dry or wet base deposition in the water could impart PAHs and impair water quality and ecology of the Soan River. Besides that, the River Soan receives about  $4 \times 10^6 \text{ m}^3/\text{y}$  of domestic and industrial wastewater from Rawalpindi and Islamabad cities. In recent years, fish production in the Soan River has been reduced from 450 to 600 tons/y due to increased pollution (Zahra et al., 2014). In the light of these facts, present study was conducted to report the status of PAHs in surface water of the Soan River. It also investigates the level of PAHs, their distribution, sources and health risk associated with PAHs.

## 2. Materials and methods

### 2.1. Study area

Soan River is the important watercourse of the Potohar region of Pakistan and is the major feeding tributary of Simly dam. It is spatially located between longitude  $71.045\text{--}73.035^\circ$  and latitude  $32.045\text{--}33.055^\circ$ . The Soan makes its origin from springs of Bun village in the Murree Hills near Pathriata, flows from east to the west and falls into the Indus River near Makhd. During its course it passes through major cities viz., Islamabad, Rawalpindi, Fateh Jung, Pindi Ghab, Talagang and Mianwali. The mean temperature of study area ranges from minimum of  $3^\circ\text{C}$  in winter to maximum of  $45^\circ\text{C}$  in summer. The river flow decrease in summer while monsoon heavy rain brings flash flooding thereby increasing runoff. Also, Soan River is fed by four tributaries including Ling stream, Kurang River, Khad Nallah and Nallah Lai. Map of the study area has been provided in Fig. S1.

### 2.2. Sampling strategy

A total of ten composite surface water samples ( $n=30$ ) from different sites were collected during summer in June 2013. Out of total ten sampling sites of Soan River, five (S5, S7, S8, S9 and S10) were on the Soan River, three sites on the Kurang River (S1, S2 and S3) one site each on Ling stream (S3) and Nallah lai (S6) (Fig. S1). The two sites (S1, S2) on the Kurang River were situated up and down stream of Rawal Dam Reservoir. Site S3 was located on Ling stream before its confluence point with Soan River at S4. Site S7 was located at Soan Camp where Kurang River and Nallah lai merges with Soan River. All the sites were located near Rawalpindi and Islamabad except S9 and S10. The latter sites were located in Dhok Pathan and Shah Muhammad Wali in Chakwal District. Description of site codes, location and activities going on in the catchment area of sites is given in Table S1.

### 2.3. Sample collection & analysis

About 5 L (in triplicate) surface water samples collected in pre-cleaned brown glass bottles from different sites (about 500 m distance from up, mid and downstream of each site). Sampling bottles were pre-washed with acetone to avoid contamination. Then, the surface water sample was combined to get a composite sample. The water sample was stored in icebox, transported and refrigerated in the laboratory at  $4^\circ\text{C}$  until analysis.

Water samples were filtered using filter (pore size 125 mm) and were solvent extracted following standard method (Separatory Funnel Liquid–Liquid Extraction, USEPA Method 3510C). Water sample (1 L) to be extracted and Dichloromethane (DCM) (25 mL) were transferred into the separating funnel. Recovery standard (naphthalene-d8; acenaphthened10; phenanthrene-d10; chrysene-d12 and perylene-d12) was added in the funnel with the sample. Funnel was shaken for 1–2 min and was vented periodically to release excess pressure. Separating funnel was allowed to settle for the separation of organic layer from the aqueous phase. The organic layer was removed after 5–10 min, and the process was repeated twice with the aqueous layer. Three of four equal portion of organic layer were collected in rotary flask after filtering from a layer of anhydrous sodium sulfate and glass wool. Rotary evaporator was used to reduce the volume of the organic layer to one and exchanged into n-hexane. The extracted samples were passed to a glass column (200 mm, 4 mm diameter) filled with 3 cm of deactivated alumina, deactivated silica of 3 cm and anhydrous sodium sulfate of 1 cm to purify the sample. Before using silica, alumina and sodium sulfate were baked in muffle furnace at  $180^\circ\text{C}$ ,  $210^\circ\text{C}$  and  $450^\circ\text{C}$  for 4 h. The column was pre-washed with n-hexane before passing the extracted layer through the column. For elution 70 mL of DCM and n-hexane at a ratio of 3:7 were used. Nitrogen stream was used to reduce the volume of elute to 0.5 mL. Before GC analysis, hexamethylbenzene (5  $\mu\text{L}$ ) was added in the elute as an internal standard.

Samples were analyzed by GC–MS (HP-5890 series II GC, HP-5972 MSD), equipped with a  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$  HP5-MS column. The chromatographic

conditions were as follows: injector temperature,  $280^\circ\text{C}$ ; ion source temperature,  $180^\circ\text{C}$ ; temperature program:  $60^\circ\text{C}$  for 2 min,  $3^\circ\text{C min}^{-1}$  to  $290^\circ\text{C}$ , and  $290^\circ\text{C}$  for 30 min. Helium was used as the carrier gas at flow rate of 1.4 mL/min. 1  $\mu\text{L}$  sample volume was injected into GC to analyze seventeen EPA PAHs which includes: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3 - c,d)pyrene (Ind), dibenzo(a,h)anthracene (dBahAn), benzo(ghi)perylene (BgHiP), coronene (Coro).

### 2.4. Quality assurance and quality control (QA/QC)

Strict quality control and quality assurance procedures were implicated throughout the sampling and analysis. Samples were extracted within seven days after sampling. Field and lab blanks were analyzed routinely with samples for possible contamination during transport, storage and analysis. No detectable PAHs were found in field and lab blanks. Naphthalene-d8; acenaphthened10; phenanthrene-d10; chrysene-d12 and perylene-d12 were used as a recovery standard with their mean recoveries calculated as follows:  $68.34 \pm 10.22$  percent,  $75.46 \pm 4.25$  percent,  $84.83 \pm 6.15$  percent,  $86.33 \pm 7.82$  percent. Limit of detection (LOD) was calculated as three times the standard deviation of the PAHs level in procedural blanks. For PAHs which were not detected in lab and field blanks, LODs were calculated as the amount of analytes per sample corresponding to the lowest calibration standard. The LODs ranged between 2.1 and 7.9 pg/L in all samples. For quantification purposes, calibration curves based on a set of six standards of concentration 5, 10, 20, 50, 100 and 200 ppb were drawn. Data acquisition and processing was controlled by Agilent MSD Productivity Chemstation software.

### 2.5. Characterization of samples

Physicochemical parameters viz., pH, total dissolved and suspended solids (TDS and TSS), electrical conductivity (EC), dissolved oxygen (DO) and total organic carbon (TOC) of water sample were determined. pH of surface water was measured by pH meter (Model no. P25). TDS and EC were recorded by TDS/EC meter (Model no. UNE-EN 61326-1) and DO with DO Meter by HACH (2968800). Total suspended solids were measured using EPA method 160.2. Total organic carbon analyzer (TOC analyzer, Analytical Jena) was used for analysis of TOC.

### 2.6. Statistical analysis

Statistical package for social science (SPSS 13.0) were applied to understand the correlation between physicochemical parameter of PAHs with their distribution pattern. Kruskal–Wallis test was applied to assess the significant differences ( $P=0.05$ ) in PAHs concentration at various sites based on the median values provided that the data was not distributed normally. Diagnostic ratios (DR) and Principal component analysis (PCA) were used to determine PAHs contamination sources. Data was standardized before PCA processing for the removal of dimensional effect on the components.

## 3. Results and discussion

### 3.1. Spatial distribution of PAHs in the Soan River

The mean concentration with standard deviation of  $\sum_{17}\text{PAHs}$  analyzed in surface water of Soan River is given in Table 1. No significant differences ( $p > 0.05$ ) were observed in the  $\sum_{17}\text{PAHs}$  concentrations at various sites located on tributaries and the main River suggesting local inputs of PAHs. The total concentration for PAHs ranged between  $61 \pm 25$  and  $207 \pm 14.8 \text{ ng/L}$ . High concentrations of PAHs at S7 is attributed to high traffic density and proximity to various petrol pumps and workshops. Moreover, Kurang River and Nallah Lai joins the Soan River at this site and drains  $4 \times 10^6 \text{ m}^3/\text{y}$  (Murtaza and Zia, 2011) of untreated domestic and industrial wastewater of various industries viz., vegetable oil processing mills, marble, soap, flour and pharmaceutical industries into the River. The presence of industries and heavy traffic around the Soan River elucidates the elevated PAHs contamination.

Based on the spatial distribution of PAHs (Fig. 1), the concentration of PAHs found to be decreased in downstream of the Soan River at S8 ( $127 \text{ ng/L}$ ). The site is located on Lahore–Islamabad Motorway where the deposition rate of PAHs in surface water of river decreased due to smooth traffic flow (Agarwal, 2009).

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