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Research paper

Toxicity and health risk assessment of polycyclic aromatic hydrocarbons in surface water, sediments and groundwater vulnerability in Damodar River Basin

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ABSTRACT

Ingestion of polycyclic aromatic hydrocarbons (PAHs) contaminated water has potential human-health and ecological consequences. A comprehensive investigation of PAHs' occurrence and distribution in the surface water and sediment samples of the Damodar River Basin was conducted using the Agilent 7890B Gas Chromatograph (GC-FID) coupled with 5977A Mass Spectrometry. The results showed that concentrations of the individual PAHs in surface water and sediments ranged from ND to 36 μg/L and ND to 582 ng/g with the highest detected levels of 3-ring PAH Acenapthylene (ACY) and 4-ring PAH Benzo(a)Anthracene (BaA) with a mean concentration of 6.12 ± 6.06 μg/L and 2.79 ± 4.5 μg/L, respectively. The concentration of 4-ring PAHs such as Fluoranthene (Flur), Pyrene (Pye), Benzo(a)Anthracene (BaA), and Chrysene (Chry) in sediment samples has mean levels of 43 ± 41 ng/g, 32 ± 29 ng/g, 52 ± 50 ng/g, and 83 ± 105 ng/g, respectively. The 4-ring PAH Chry was frequently detected in all sediment samples, while the 3-ring PAH ACY was dominant in surface water samples. The principal component analysis (PCA) and diagnostic ratios suggested that the PAHs contamination in surface water was due to petrogenic and fuel combustion. In sediments, PAHs' primary sources were coal burning, fuel combustion, petrogenic, and pyrolysis. The incremental lifetime cancer risk (ILCR) for children and adults due to ingestion of surface water ranged from ND to 4.25×10^{-5} and ND to 7.21×10^{-5}, respectively. In contrast, the Risk index (RI) values ranged from 4.3×10^{-5} and 7.3×10^{-5}. For sediment samples, higher toxic equivalent quotient (TEQ = 1865 ng/kg) and mutagenic equivalent quotient (MEQ = 1665 ng/kg) for eight carcinogenic PAHs indicate extremely high toxicity. Improper management of mine drainage, frequent flooding of open cast mines, and hydraulic connection between the surface water, sediments, and groundwater significantly deteriorated overall water quality in the DRB.

1. Introduction

The polycyclic aromatic hydrocarbons (PAHs) occur naturally in coal, crude oil, and gasoline while others are manufactured. Two of the primary natural sources of PAHs include wild forest fire and volcanic eruptions (Liu et al., 2014). Some PAHs are the byproduct of anthropogenic activities such as PAHs released due to incomplete combustion of PAHs containing substances coal, oil, gas, creosote, plastics, pesticides, dyes, wood, garbage, and tobacco. Additional anthropogenic input includes oil spills, urban runoff, incomplete combustion, domestic and industrial wastewater discharges, vehicle exhaust, and industrial emissions (Boonyatumanond et al., 2006; Zakaria et al., 2002; Adeniji et al., 2019a). The PAHs are ubiquitous in the environment and often detected in various environmental matrices, including soil, water, sediments, and aquatic microorganisms (Countway et al., 2003; Chen et al., 2004; Cheollee et al., 2005; Wang et al., 2018; Stout et al., 2004). The petrogenic and Pyrogenic PAHs were most abundant and generally formed by the reduction of biogenic precursors (Tongo et al., 2017; Xiao et al., 2014).

Low molecular weight (LMW) PAHs' typical molecular structure comprises more than one fused aromatic ring of carbon and hydrogen atoms. While the higher molecular weight (HMW) PAHs comprised of

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four or more benzene rings and are far more stable and persistent than the LMW PAHs. To date, approximately 200 such compounds have been detected in various environmental compartments. PAHs are hydrophobic and lipophilic, making them susceptible to adsorption on the suspended particulates in the aquatic environment. Studies have reported that high PAHs deposits on soil and estuarian, lake, and marine sediments could exert toxic effects on aquatic biota (Tolosa et al., 2004; Brazkova et al., 2013; Olatunji et al., 2014). Due to their higher toxicity, mutagenic, and carcinogenic potential, PAHs are of critical environmental concern. The toxicity of PAHs depends on the type of species, molecular structure, and exposure routes (Douben, 2003). For example, oral intake of PAHs through food, inhalation, and dermal interaction causes a significant risk to human health. Such exposures could result in severe short and long-term health effects, including some major cardiovascular and respiratory diseases (Adeniji et al., 2019; Perez-Padilla et al., 2010). Based on PAHs' toxicity, the United States Environmental Protection Agency (USEPA) has declared sixteen PAHs as priority pollutants.

The rapid growth of industrialization has increased the daily emission of PAHs (Lang et al., 2008; Zhang and Tao, 2009). For example, developing countries like India and China have witnessed a steady increase in the environmental releases of PAHs. In 2004, three countries accounted for the maximum global atmospheric emission of USEPA's 16 priority PAHs; they are China (114 Gg y^{-1}), India (90 Gg y^{-1}), and the United States (32 Gg y^{-1}) (Zhang and Tao, 2009). Studies on PAHs exposure in Hooghly and Brahmaputra River, India (Khuman et al., 2018), Algoa Bay, South Africa (Adeniji et al., 2019a), Buffalo River Estuary, South Africa (Adeniji et al., 2019), Gomti river, India (Malik et al., 2011) have raised serious concern on exposure to PAHs and resulting in adverse human health impacts. In recent years, in India, river water pollution has become one of the most significant issues. Due to the rapid industrialization and urbanization, increased river water pollution in India is routinely reported.

The Damodar River basin (DRB), which includes many industries, has witnessed large-scale water pollution. The DRB is a seasonal water system situated in the mineral-rich area of the Chotanagpur plateau. It receives both regulated and unregulated discharge from various industries, including wastewater discharge from the steel industry, coal washery, mining, and coke industry. Few studies have documented widespread pollution in the DRB, including heavy metal contamination, soil erosion, and deteriorating water overall water quality. For the first time in this manuscript, we document the occurrence, distribution, and human and ecological risk assessment due to PAHs pollution in the DRB. The DRB serves as a critical water resource for millions of inhabitants in the Jharkhand and West Bengal area who use water for domestic and agricultural purposes. Given the importance of DRB, we have decided to study the sources of pollution, and the resulting impact on surface water, sediments, and groundwater need to be evaluated. In this manuscript, we have chosen PAHs as a primary pollutant due to the nature of industries located in the areas, large-scale coal mining activities, and the inhabitants' general lifestyle. We have documented the analysis of extensive surface water and sediment samples and evaluated groundwater vulnerability in the region.

2. Materials and methods

2.1. Study area

The DRB is in one of the major industrial areas surrounded by four large coalfields: Jharia, North Kanakpura, East Bokaro, and Raniganj. Besides coalfields, it is also home to several large thermal power plants, captive steel plants, and coal mines. The location of DRB is ideally suited to investigate the occurrence of PAHs in surface water, sediments, and groundwater. The DRB lies between 22°N and 24°N latitude and 84°E to 88°E longitude covering approximately 23,170 km^2 areas. Damodar River is the central part of the basin and millions of people living in the adjoining area use river water of the DRB for drinking and agricultural purposes. The Damodar River, situated in Eastern India at elevation 1068 m, is a small rain-fed perennial river originates from the Chhotanagpur hill/Khamerpet hill. The total length of Damodar River is 541 km, out of which it 240 km in the state of Jharkhand while the remaining flows in West Bengal before finally merging into the Bay of Bengal (BoB). Besides the Damodar River, the DRB has several tributaries and sub tributaries, such as Garga Nalla, Barakar, Konar, Khudia, Jamunia, Katri, Tamna Nalla, and Noonia. It also has five reservoirs, of which two are located on the Barakar River at Tilaiya and Maithon, two on Damodar River at Tenughat and Panchet, and one on Konar River (Fig. 1). Damodar River receives the discharge from large-scale industries in the area, and unprecedented levels of mining activities further challenged the rivers' assimilation capacity. Not surprisingly, the Damodar River is one of India's most polluted rivers (Singh et al., 2008; Singh and Hasnain, 1999; Tiwary, 2001).

The DRB is the repository of approximately 46% of India's entire coal reserve. Large-scale coal mining activities in this area increase the net pollution load on the Damodar River and the underlying groundwater (Tiwary and Dhar, 1994). Improper management of mine water affects the surface water quality of the Damodar River. According to one estimate, nearly 50% of the discharged effluent from coal mine water ends up in the Damodar River. Additionally, a series of coal washeries located on the riverbank often discharge polluted water containing fine coal particles, thereby impacting the sediment quality. Many studies have documented the impact of mine drainage on surface and groundwater quality. These studies mainly focused on the occurrence of ions, total dissolved solids, trace elements, and water quality parameters to assess mining activities' net impact on groundwater resources. In this study, we have focused on PAHs' occurrence in surface water and sediments in the Damodar River, impacted by industrial activities and mine drainage originating from several coalfields.

2.2. Sampling and pretreatment

A total of (n = 108) samples, including 54 sediment samples and 54 surface water samples, were collected in the pre-monsoon season (February to April 2019). Sediment samples were collected using a stainless steel van Veen grab sampler (AISI 316 station steel, the grab = 8 mm arms, manufactured from the square tube, 60 × 60 × 4 mm with 12 mm reinforcements) from 5 cm to 7 cm depth and were packed in 2 kg capacity polythene bags. The surface water samples were collected from half meter depth directly from the river using screw cap glass bottles (2 L). Before sampling, the containers were thoroughly washed with diluted nitric acid (10%) and deionized water to prevent potential cross-contamination during sample handling and were rinsed with the respective samples during sampling (Salaudeen et al., 2018). Four subsamples of 1-liter capacity have been collected from the basin at four different points to obtain the representative water samples. The subsamples were mixed in a steel bucket, and a fixed quantity of 1-L sample was taken. Four sediment subsamples were collected from the basin near the sites in a random manner to form representative samples. To preserve the samples, they were kept in the icebox and transferred to the laboratory within 10 h. The semi-solid samples were kept in the refrigerator at −16 °C until analysis. The water samples were stored in the refrigerator at – 3 °C for further analysis.

2.3. Extraction, clean-up, and analysis of PAHs from samples

For 16 PAHs Naphthalene (NA), Acenaphthene (AC), Acenapthylene (ACY), Fluorene (Fluor), Phenanthrene (Phen), Anthracene (AN), Fluoranthene (Flur), Pyrene (Pye), Benzo(a)Anthracene (BaA), Chrysene (Chry), Benzo(b)Flouranthene (BbF), Benzo(k)Flouranthene (BkF), Benzo(a)Pyrene(BaP), Dibenzo[a,h]anthracene (DA), Benzo[g,h,i]perylene (BgP) and Indeno[1,2,3-cd]pyrene (IN) extraction from surface water samples, we followed a well-established procedure presented in

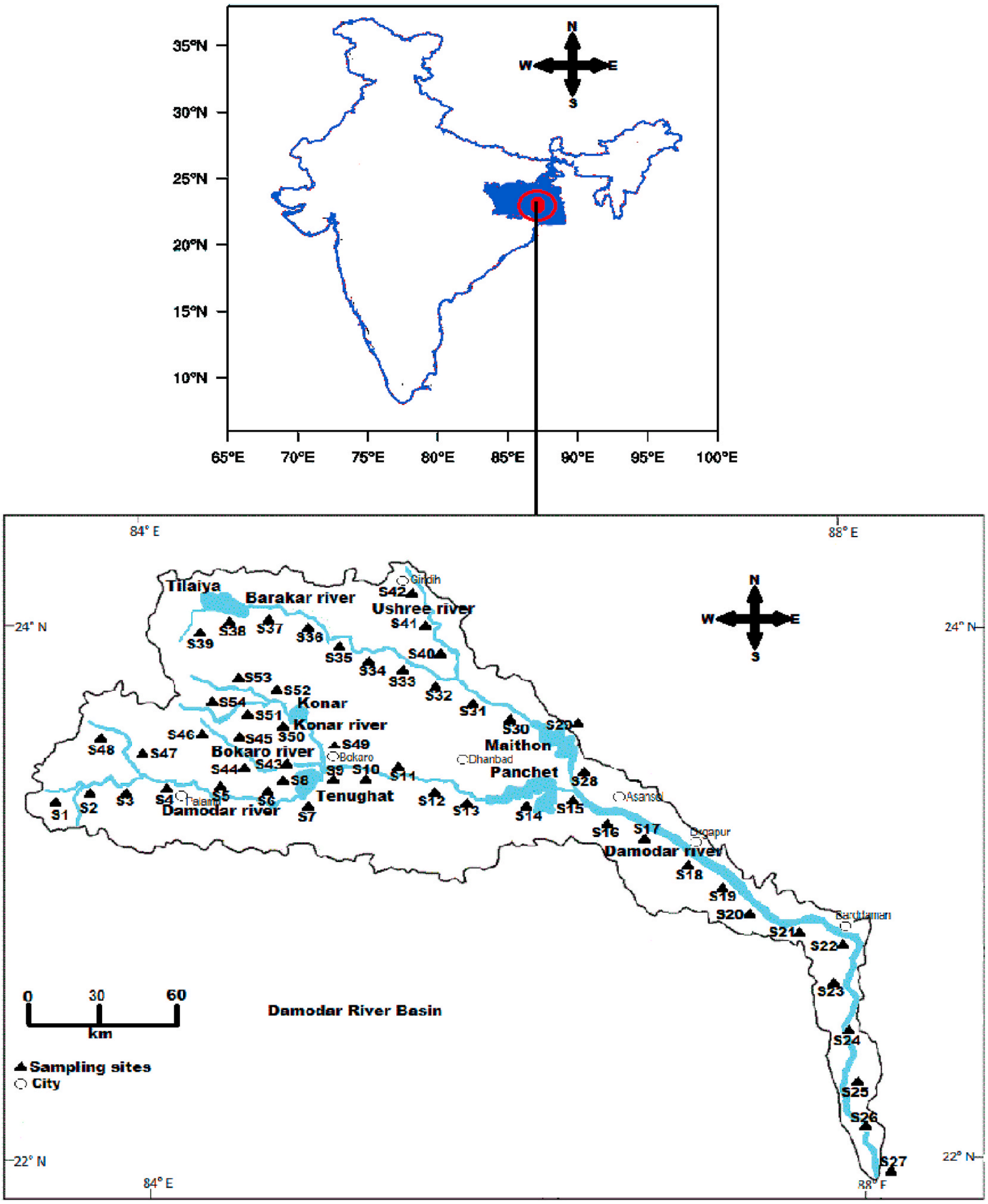


Fig. 1. The surface water and sediment sample collection sites of Damodar Basin.

the study by Chakraborty et al. (2016a). Dichloromethane (DCM) was used for liquid-liquid extraction (three times: 50, 25, 25 mL) with 1 L of water samples. The organic phase was then separated and collected by mixing 10 g sodium chloride and shaking it for 4–6 min. This procedure was repeated three times, and finally, the combined organic phase was collected. The drying process started by passing it through sodium sulfate placed on 3 cm thick glass wool. A rotary evaporator (Hei-VAP Core - hand lift model with G1 diagonal glassware) was used for concentrating the extract. A standard solvent extraction procedure was used to extract PAHs from sediment samples. The dry samples were collected, homogenized, properly cultured, and kept for the sample preparation. This process included mixing 2 g of dry solid sample with 0.5 g anhydrous Na_2SO_4 and was sonicated using 10 mL of DCM for 1 h followed by centrifugation. A 3 ml of supernatant was filtered through 2 g of silica gel column with 11 ml 1:1(v/v) elution of hexane and DCM (Chen et al., 2007). The evaporation of solvent fractions was carried out with exchanging by acetonitrile with a final volume of 2 ml.

Radiolabeled standards of PAHs (Naphthalene-D8, Phenanthrene-D10, and Chrysene-D12) were used as surrogate standards. For sample extraction, a silica gel glass column (30 cm long and 3 cm diameter glass) filled with 10 g activated silica gel and 5 g anhydrous Na2SO4 was used. The PAHs were eluted using 100 mL of DCM and n-hexane mixture (1:1, v/v). Finally, under a gentle stream of pure nitrogen, the eluent solvent was concentrated to 20 μL. The analytes were quantified by adding an internal standard of Hexamethyl benzene before analysis (Khuman et al., 2018). Extracted water and sediment samples collected from the DRB were analyzed to detect the USEPA's 16 priority PAHs. The analytical quantitation was carried out using the Agilent 7890B Gas Chromatograph (GC-FID) system equipped with the flame ionization detector (FID). The system is coupled with 5977A Mass Spectrometry equipped with an HP-5 MS capillary column (30 m × 0.32 mm × 0.25 μm) with a 7-inch cage. Because of the low sensitivity of the single GC system, we utilized the GC system coupled with the MS system, which has its stand-alone detector. While using the MS system, we only relied on the detector associated with the MS system. In splitless mode, 1 μl of each sample was injected. High purity nitrogen gas was used as a carrier gas at a flow rate of 1.83 mL/min. In the beginning, the oven temperature was set at 70 °C for 1 min and then increased to 300 °C at a rate of 5 °C min^{-1} over 20 min. The Temperature of the injector and transfer line were maintained at 300 °C and 325 °C, respectively.

2.4. Quality assurance and quality control

For quality assurance and quality control, field blank samples and sample duplicates were collected. The samples spiked with radiolabeled surrogate standards (Phenanthrene-D10, Naphthalene-D8, and Chrysene-D12) were used as an internal standard for calibration of all species of PAHs. The quality control for PAHs analysis was ascertained from these samples. The recovery percentages of 16 PAHs in water and sediment samples were approximately 90–100% and 85–95%, respectively. The method detection limits (MDLs) of the target PAHs were calculated as three times the standard deviation (SD) plus the mean concentrations of target compounds in blank samples. The MDLs of the target PAHs for sediment and surface water samples were 1 ng/g and 0.1 μg/L, respectively. The laboratory and field blanks were extracted and analyzed in the same way as the samples. The concentration of PAHs less than the method detection limits was deemed as non-detect (ND).

2.5. Health risk assessment

For human health risk assessment, the possibility of adverse health effects due to exposure to carcinogenic substances over a specific duration was evaluated for two sets of population groups - adults and children (US EPA 2001; Gerba 2006; US EPA 2009). In this study, the lifetime average daily dosage (LADD) (mg/kg/day) (Equation (1)), incremental lifetime cancer risk (ILCR) (Equation (2)), and risk index (RI) (Equation (3)) were carefully estimated. The carcinogenic risk was evaluated for the ingestion of PAHs contaminated water. For calculating LADD, typical values available in the literature were used. The LADD equation can be written as:

$$\text{LADD}\ (\text{mg/kg/day}) = (\text{C} \times \text{SA} \times \text{KP} \times \text{ET} \times \text{EF} \times \text{ED} \times \text{CF}) / (\text{BW} \times \text{AT}) \tag{1}$$

where.

C – Concentration of pollutants in the water samples (mg/L).
SA – Exposed skin area.
KP – Coefficient of dermal permeability.
ET – Exposure time.
EF – Exposure frequency.
ED – Exposure duration.
CF – Unit conversion factor.
BW – Average body weight.
AT – Averaging time.

For calculating LADD, two age groups (30 years: adult and 6 years: child) were considered representative populations. The LADD equation's typical values include average body weight of 70 kg for adults and 15 kg for a child, respectively (US EPA 1989, 2004, 2015; ATSDR 2005; Gerba 2006; DTSC 2014; Adeniji et al., 2019). The ILCR and RI were calculated using equations (2) and (3) following the USEPA guidelines (US EPA 1989; 2015; Adeniji et al., 2019a). The cancer slope factors (CSF) for different PAHs congener were obtained by multiplying the toxic equivalent factor (TEF) for each PAHs by the CSF of BaP (7.3 mg/kg/day) (US EPA, 2015; IARC 2006; Kumar et al., 2015).

$$\text{ILCR} = \text{LADD} \times \text{CSF}(\text{Cancer}\ \ \text{Slope}\ \ \text{Factor}) \tag{2}$$

$$\text{RI} = \Sigma\ \text{ILCR} \tag{3}$$

$$\text{TEQ} = \Sigma\ \text{C}_{\mathbf{n.TEFn}} \tag{4}$$

$$\text{MEQ} = \Sigma\ \text{C}_{\text{n.}}\ \text{MEF}_{\text{n}} \tag{5}$$

For the sediment samples collected from the DRB, the toxic equivalent quotient (TEQ) and mutagenic equivalent quotient (MEQ) were calculated using equation (4). Potential mutagenic and carcinogenic toxicities of the HMW PAHs were assessed relative to the BaP. In equations (4) and (5), Cn stands for each PAHs congeners (n) concentration, TEFn represents each PAHs congeners (n) toxic equivalent factor, and MEFn represents each PAHs congeners (n) mutagenic equivalent factor, respectively. These values were calculated by multiplying with their mutagenic equivalent factor (MEQ) or toxic equivalent factor (TEQ) with the summation of all sediment samples carcinogenic PAHs concentration (CCME 2010; Lerda 2011; Adeniji et al., 2019).

3. Results and discussion

3.1. PAHs concentration in surface water and sediments

The concentration of 16 PAHs in surface water and sediments of the DRB were summarized in Table 1. Except for the BaP, DA, and IN, all PAHs were detected in water samples with a total mean concentration of 10.11 μg/L and a total standard deviation of 11.59 μg/L. In the DRB water samples, PAHs' total concentration ranged from ND (not detect) to 36 μg/L. The three-ring PAHs were more dominant in water samples, followed by the four rings PAHs and contained about 67% and 28% of the total PAHs concentration. The three-ring PAHs ACY and four-ring PAHs BaA were dominant in most surface water samples. A high concentration of these LMW PAHs could be attributed to the high coal mining in the DRB's valley. This observation is consistent with the findings documented in numerous studies that reported large-scale mining activities and widespread PAHs pollution in soil, sediments, and water bodies. The high concentration of PAHs in the coal mining areas is well documented, as evidenced by numerous studies. For example, studies conducted by Ouyang et al. (2018) have documented the presence of varying levels of three/four-ring PAHs (including 16 priority PAHs) in soil and sediments of coal mining subsidence areas in Huainan, China. The authors attributed the occurrence of PAHs in the surface sediments to the hydrogeological condition of the mining area.

Similarly, studies conducted by Liu et al. (2012) reported extensive PAHs pollution in the Tiefa coal mine district, Liaoning, China. The authors reported widespread PAHs contamination in the mining zone soils, agricultural and lake bank soils in the surrounding area of the Tiefa

Table 1
PAHs concentration in surface water (μg/L) and sediments (ng/g) of Damodar Basin.

PAHs	Water			Sediment		
	Min	Max	Mean ± SD	Min	Max	Mean ± SD
NA	ND	1.08	0.38 ± 0.29	ND	61	19 ± 16
AC	ND	0.91	0.29 ± 0.23	ND	103	25 ± 20
ACY	ND	36	6.12 ± 6.06	3	79	16 ± 11
Fluor	ND	0.81	0.24 ± 0.19	ND	100	19 ± 17
Phen	ND	0.29	0.07 ± 0.07	ND	39	12 ± 7
AN	ND	0.36	0.12 ± 0.08	ND	21	5 ± 4
Flur	ND	0.08	0.005 ± 0.01	ND	280	43 ± 41
Pye	ND	0.13	0.02 ± 0.03	9	190	32 ± 29
BaA	ND	23	2.79 ± 4.5	ND	366	52 ± 50
Chry	ND	0.19	0.02 ± 0.04	ND	582	83 ± 105
BbF	ND	0.21	0.02 ± 0.04	ND	154	27 ± 24
BkF	ND	0.25	0.05 ± 0.07	ND	52	7 ± 7
BaP	ND	ND	ND	ND	27	9 ± 7
DA	ND	ND	ND	ND	69	15 ± 10
IN	ND	ND	ND	ND	46	8 ± 9
BgP	ND	0.07	0.003 ± 0.01	ND	38	8 ± 8
Total	ND	36	10.11 ± 11.59	ND	582	380 ± 365

*ND= Not detected.

coal mine. Through PCA analysis, the authors concluded that extensive mining activities in this area with PAHs pollution originating from unburned coal (19.8%) and coal gangue (26.7%). While PAHs pollution is mostly attributed to combustion sources, the environmental impact of native hard coal is not fully understood. According to Achten and Hofmann (2009), unburnt hard/bituminous coal contains anywhere between hundreds to thousands of mg/kg of PAHs. The macromolecular and mobile phase of the hard coal containing PAHs is of particular concern due to its mobility and likelihood of its release during fugitive airborne emission, accidental releases, natural erosion of coal seams, coal preparation and washing, dumping of tailings, loading operations, and slumping and runoff from the storage area poses a more significant threat to the aquatic environment.

In this study, the water samples (S30) and (S36) collected at the Barakar River of the DRB showed a higher concentration of ACY, and BaA with a maximum concentration of ACY and BaA were found as 36 μg/L and 23 μg/L (Fig. 2). The dominance of 3 ring ACY in this study shows similarity with other studies in India, Gomti River (Malik et al., 2009), Brahmaputra, and Hooghly River (Khuman et al., 2018). The concentration ranges of PAHs in surface water found in this study were higher than the concentration of PAHs reported at Brahmaputra and Hooghly River, India (Khuman et al., 2018), Xiamen Harbor, China (Zhou et al., 2000), Ulsan Bay, Korea (Khim et al., 2001) and Gao-Ping River, Taiwan (Doong and Lin, 2004) (Table 2). The concentration of PAHs in the Gomti River, India (Malik et al., 2011) is higher than the concentration reported in this study (Table 2). The absence and low concentration of HMW PAHs in this study are similar to the other studies reported by Gao-Ping River, Taiwan (Doong and Lin, 2004), and Brahmaputra and Hooghly River, India (Khuman et al., 2018). The HMW PAHs (5 and 6 ring) were not detected frequently and mostly absent in water samples, as they remained adsorbed to sediments due to their non-biodegradable, nonvolatile, and less water-soluble properties (Jiries et al., 2000).

The PAHs concentration in sediment samples showed a wide range of

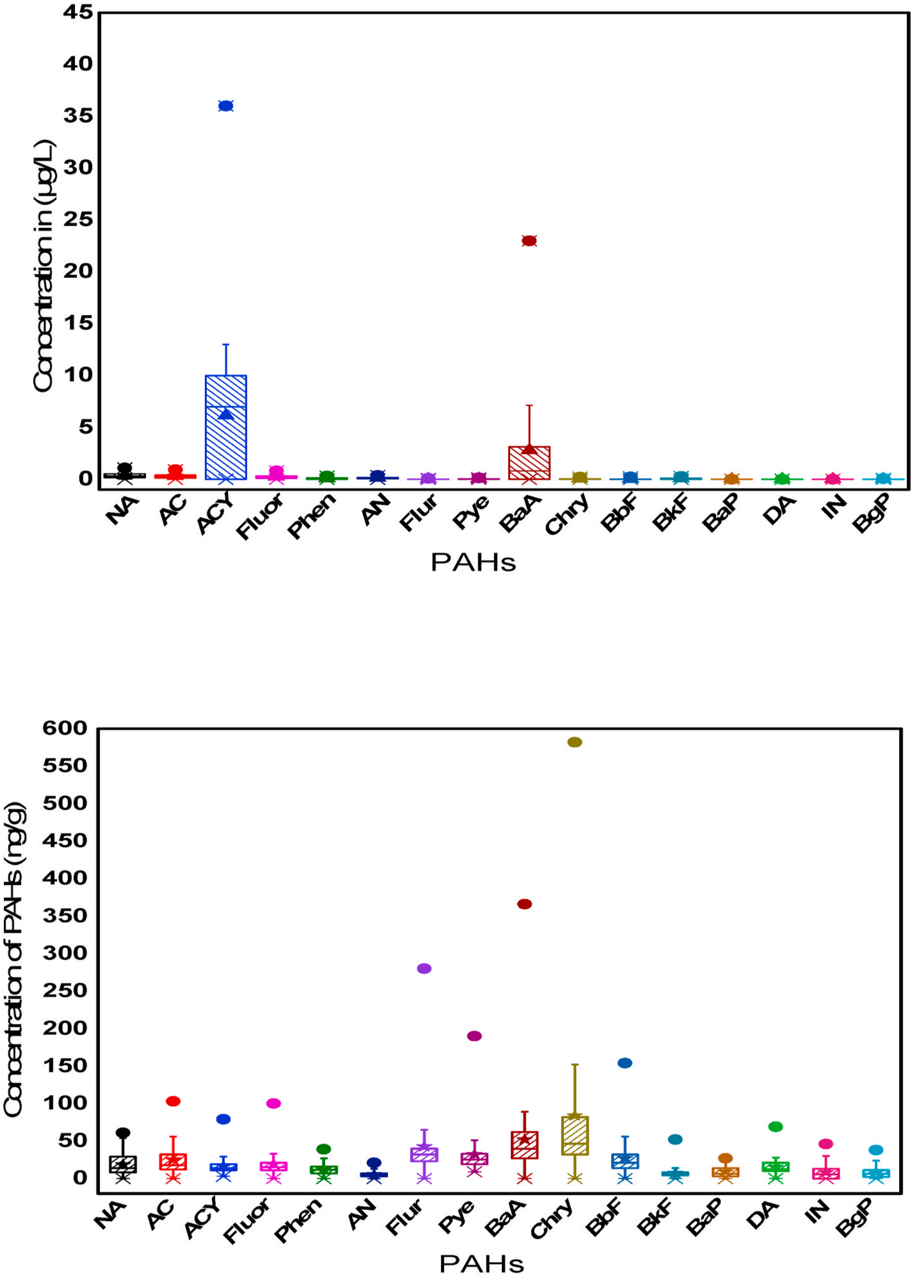


Fig. 2. The levels of various PAHs in surface water and sediments of Damodar Basin.

Table 2
Comparison of PAHs levels in water and sediment with earlier studies.

Study area	No. of PAHs studies	PAHs range		References
		In water (ng/L)	In sediment (ng/g)	
Dalio river watershed, China	18	946–13449	62–841	Wei and Mengchang (2007)
Gao-ping river, Taiwan	16	Oct-00	8–356	Doong and Lin (2004)
Gomti river, India	16	0–84000	5–3723	Malik et al. (2011)
Hoogly and Brahmaputra river, India	16	0–30000	0–636	Khuman et al. (2018)
Kor river, Iran	16	45–375	167–530	Farshid and Amir (2011)
Liaohe river basin, china	16	0–615	0–60057	Yang et al. (2014)
Songhua river, china	16	164–2746	68–654	Xuesong and Jing (2014)
Tonghui river, china	16	192.9–2651	127–928	Huang (2004)
Ulsan Bay in Korea	16	ND-200	17–3100	Khim et al. (2001)
Xiamen Harbor in China	16	100–900	247–480	Zhou et al. (2000)
Damodar basin, India	16	0–36000	0–582	This study

variations, and almost all 16 PAHs were detected in sediment samples, among which Chrysene was the most dominant PAH compound that accounted for around 22% of the Σ16 PAHs mean concentration. The detected concentrations of PAHs for 2-ring, 3-ring, 4-ring, 5-ring, and 6-ring accounted for approximately 5%, 20%, 55%, 15%, and 4% of the mean concentrations of Σ16 PAHs, respectively. The total PAHs concentration ranged from ND (not detected) to 582 ng/g with a higher concentration of 4-ring PAHs. The samples from S23 to S42 were rich in 4-ring PAHs, and a concentration of 582 ng/g was detected at the sampling site S35 at Barakar River, one of the high coal mining areas. The Σ16 PAHs Mean ± SD is 380 ± 365 ng/g with an individual higher concentration of PAH Chry 83 ± 105 ng/g followed by BaA 52 ± 50 ng/g. The box plots clearly show the number of variations of PAHs concentrations in sediments with a higher value of standard deviation and concentration of the 4-ring PAHs (Fig. 2). The toxic PAHs like BaA, Chry, BbF, and DA were found in higher concentration than the other toxic PAHs with mean values of 52 ± 50 ng/g, 83 ± 105 ng/g, 27 ± 24 ng/g, and 15 ± 10 ng/g. In this study, the concentration of Σ16 PAHs in the sediment samples was lower than the concentration reported by similar studies in other riverine sediments, such as the Dalio river watershed, China (Wei and Mengchang, 2007), Gomti river, India (Malik et al., 2011), Liaohe river basin, China (Yang et al., 2014), Tonghui river, China (Huang, 2004) and Ulsan Bay, Korea (Khim et al., 2001) (Table 2). PAHs in the DRB were comparable with riverine sediments from the Hooghly and Brahmaputra River, India (Khuman et al., 2018), Kor river, Iran (Farshid and Amir, 2011), Songhua river, china (Xuesong and Jing, 2014). However, they were more than the concentration reported from the Gao-ping river, Taiwan (Doong and Lin, 2004), and Xiamen Harbor in China (Zhou et al., 2000) (Table 2).

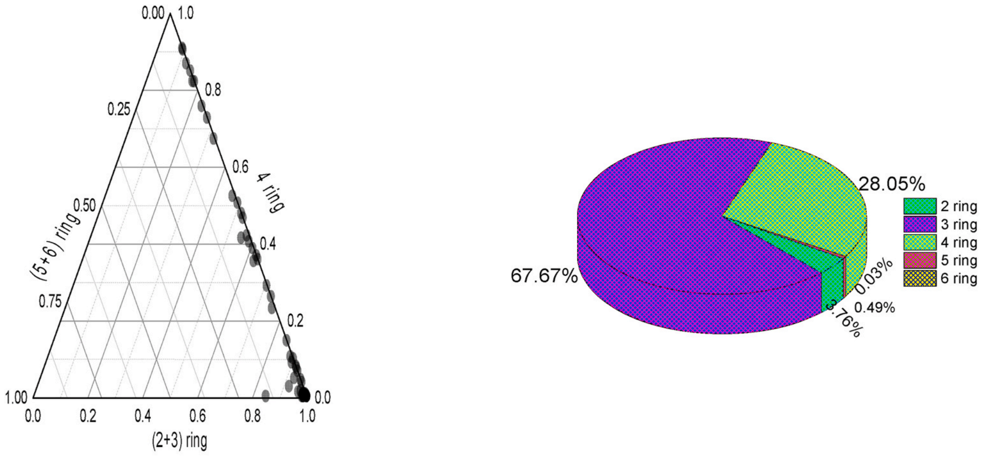
3.2. *Assessment of groundwater pollution vulnerability to PAHs*

Various studies have documented the adverse effect of mining activities on the groundwater resources at the DRB. Most of these studies focused on assessing groundwater quality parameters such as pH, total dissolved solids, turbidity, conductivity, and sulfate. The presence of various PAHs in the surface water and sediments in the DRB, as discussed earlier, can potentially impact groundwater in the DRB. Three primary processes are responsible for PAHs' potential contamination of groundwater in the DRB: flooding of the Damodar river, discharge of washery effluents, and induced recharge through direct hydraulic connection. The sorbed PAHs will remain confined to the sediments, while the direct hydraulic connection between the groundwater and river water could transport hydrophilic PAHs to the groundwater resources. Particularly during the river stages, higher stages will artificially induce groundwater recharge, thereby transporting PAHs to the groundwater proximal to the wells in the DRB. Series of pumping tests and modeling of aquifer-stream water interaction using Groundwater Modeling System software showed that Damodar River stages impact the groundwater flow in the DRB (Roy et al., 2015).

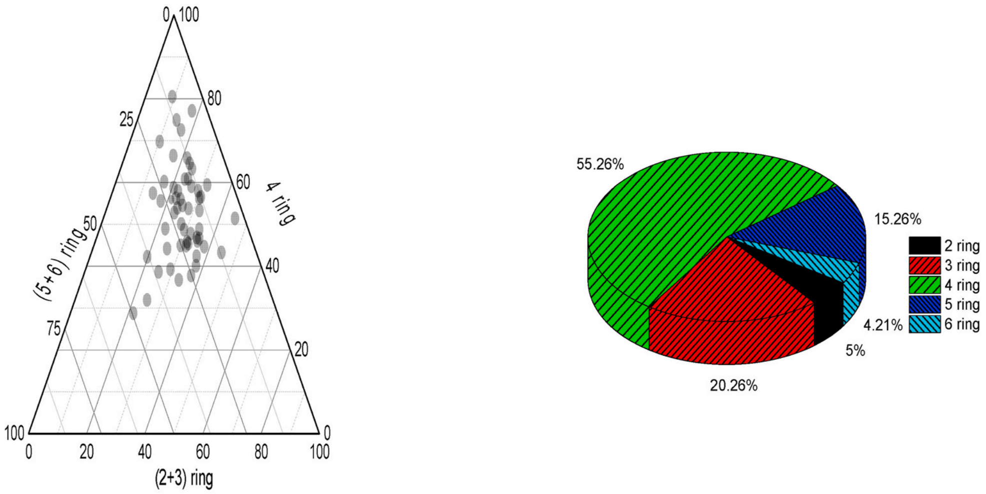
The groundwater at the DRB is increasingly vulnerable to various pollutants, including PAHs. Studies have shown that the groundwater in contact with coal-bearing sediments is also vulnerable to coal mining drainage, potentially enriching the groundwater with trace metals (Mohanty et al., 2018). While the authors have indicated the groundwater vulnerability to pollution from mine drainage, other contributory factors such as surface runoff potentially negate the adverse impact. Similarly, Singh et al. (2008) demonstrated that groundwater in the DRB area is indeed impacted by mining and other associated activities (excavation and dumping). The vulnerability of groundwater pollution due to PAHs in the DRB cannot be understated. Studies have shown PAHs in the groundwater samples collected from the coal mine in Henan Province, China (Wang et al., 2009a,b). The authors have demonstrated that the LMW PAHs such as naphthalene, phenanthrene, fluorene, and chrysene were predominant in the groundwater samples. Similar results were also reported by Chen et al., 2019 documenting extensive PAHs in the groundwater samples collected from six mines in Xuzhou, China. The high concentration of LMW PAHs and its subsurface mobility is a cause of concern due to its potential threat to groundwater resources. Studies conducted by Liu et al. (2012) in the Tiefa coal mining area showed that extensive mining activities and poor coal mine waste management adversely affect water resources. Improper mine waste management such as dumped spoil tips, coal gangue, coal dust, unburned coal, and weathering & leaching in the mining areas contaminate the surrounding soils with PAHs and vertically mobilizes the LMW PAHs, thereby threatening the groundwater resources. It is particularly true for the high solubility LMW-PAHs that deposits on the soil particulate matter that may eventually reach the shallow aquifer contaminating the groundwater Liu et al. (2012). For the first time, we document the presence of a high concentration of low molecular weight PAHs in the DRB. We also observed a high concentration of LMW PAHs in the samples taken from and near the coal mining areas. The evidence clearly shows a causal relationship between the coal mining activities in the area and the PAHs' occurrence, distribution, and the likelihood of groundwater pollution in the DRB. Groundwater in the DRB is a valuable resource, and as such, contamination of this resource due to LMW PAHs originating from intensive coal mining operations in the region deserves serious consideration.

3.3. *PAHs composition*

The 16 PAHs are generally characterized by low (2+3-ring), middle (4-ring), and higher (5+6-ring) molecular weight PAHs. The compositional diagrams of PAHs in surface water and sediments of the DRB are shown in Fig. 3. It shows that the lower and middle ring PAHs were most abundant in surface water and sediment samples. In general, 2-ring PAHs were dominant in surface water samples. Of the total Σ16, PAHs mean concentrations, the 2-ring, 3-ring, and 4-ring accounted for 3%, 28%, and 67% concentration. The higher concentration of LMW PAHs in surface water samples may be due to their high aqueous solubility and high vapor pressure (Xu et al., 2014). On the contrary, the HMW PAHs compounds with low water solubility and hydrophobic nature tend to adsorb on sediments and suspended particulate matter (Li et al., 2006). The PAHs in sediment samples mainly composed of 3-ring, 4-ring, and 5-ring but the 2-ring and 6-ring PAHs contribute a less amount towards



Composition in water



Composition in sediments

Fig. 3. Ternary diagram and pie-chart for the ring wise composition of different PAHs in water and sediments of Damodar Basin.

the total PAHs concentration. The PAHs of 2-ring, 3-ring, 4-ring, 5-ring, and 6-rings contribute 5%, 20%, 55%, 15%, and 4% towards the Σ16 PAHs mean concentration, respectively (Fig. 3). Compared to the PAHs concentrations in the surface water samples, the higher ring PAHs were more dominant in the sediment samples due to their non-biodegradable, nonvolatile, and less water-soluble properties (Jiries et al., 2000).

3.4. PAHs source identification

3.4.1. Diagnostic ratio

The concentration ratios or molecular ratios of some selected PAHs are widely used for identifying the sources (Yunker et al., 2002). The primary sources of PAHs contamination are petrogenic, pyrogenic, and diagenetic sources. The PAHs concentration ratios such as FIA/Py, PhA/An, An/An + Ph, FIA/(FIA + Py), BaA/BaA + Chy and IP/(IP + BghiP) (Liu et al., 2008), BaA/(BaA + Chyr) (Wang et al., 2007), Bap/B(g,h,i)P (Wang et al., 2010), AN/(AN + Phen), Flur/(Flur + Pye) (Chakraborty et al., 2016b) have been used in environmental samples as distinct chemical tracers to identify possible sources of PAHs. In this study, PAHs sources in water and sediment samples are determined from AN/(AN + Phen) Vs. Flur/(Flur + Pye), and IN/(IN + BgP) Vs. BaA/(BaA + Chry) ratios (Table 3). In Fig. 4, the 85% ratios of AN/(AN + Phen) were >0.1, and 15% of ratios were <0.1, which suggested a source of combustion and petroleum origin. The 93% ratios of Flur/(Flur + Pye) were <0.4 which showed a petrogenic origin, 2% of ratios from 0.4 to 0.5 and >0.5 which suggested fuel combustion and coal, grass, wood burning. In this study, 37% ratios of BaA/(BaA + Chry) were <0.2, and 63% of ratios were >0.35, which showed the source of PAHs at DRB is petrogenic and fuel combustion. Thus 100% ratios of IN/(IN + BgP) were less than < 0.2, which showed a petrogenic origin.

For the sources of contamination in sediment samples, the ratios of AN/(AN + Phen) Vs. Flur/(Flur + Pye) and IN/(IN + BgP) Vs. BaA/(BaA

Table 3

Guidelines for PAHs Diagnostic Ratios considered for identifying sources of PAHs in the DRB water and sediments samples.

PAHs Molecular Ratios	Diagnostic Ratio	Sources	Reference
AN/(AN + Phen)	<0.1	Petrolum	Chakraborty et al. (2016b)
	>0.1	Combustion	
Flur/(Flur + Pye)	<0.4	Petrogenic	Zhu et al. (2008)
	0.4–0.5	Fuel combustion	
	>0.5	Coal, grass, and wood burning	
BaA/(BaA + Chry)	<0.2	Petrogenic	Wang et al. (2007)
	0.2–0.35	Fuel combustion	
	>0.35	Coal, grass, and wood burning	
IN/(IN + BgP)	<0.2	Petrogenic	Tobiszewski (2014)
	0.2–0.5	Fule combustion (crude oil or vehicular emission)	
	>0.5	Coal, grass, and wood burning	

+ Chry) was used. However, the ratio of AN/(AN + Phen) $>$ 0.1 indicates combustion, and a ratio$<$0.1 the source of PAHs are generally petroleum sources. The Flur/(Flur + Pye) ratios of 0.5 are considered as the transition point of combustion/petroleum. The Flur/(Flur + Pye) ratios $>$0.5 shows a pyrolytic source and ratios of Flur/(Flur + Pye) $<$ 0.5 considered as an origin of petrogenic source (Zhu et al., 2008). The ratios of IN/(IN + BgP) $<$ 0.5 suggested a petrogenic origin and the ratios $>$ 0.5 indicates coal, gross, and wood combustion origins, the ratios of BaA/(BaA + Chry) a ratio $<$ 0.2 showed petrogenic origin, ratios $>$ 0.35 suggested pyrogenic sources, and the ratios between 0.2 and 0.35 showed a mixed source (Yunker et al., 2002). The scatter plots for water and sediment samples were used for identifying the emission sources of PAHs (Fig. 4). In Fig. 4 the 89% ratios of AN/(AN + Phen) were $>$0.1 and 11% of ratios were $<$0.1, which showed a combustion and petroleum sources, the 63% ratios of Flur/(Flur + Pye) were $>$0.5, 31% were $<$0.5 and 5% of ratios were equal to 0.5 which showed a source of pyrolytic origin, petrogenic origin and transition point of combustion/petroleum, respectively. The 68% ratios of BaA/(BaA + Chry) were $>$0.35. 16% of ratios were from 0.2 to 0.35, and 15% of ratios were $<$0.2, which suggested a source of pyrogenic origin, mixed sources, and from the petrogenic origin. Furthermore, 61% ratios of IN/(IN + BgP) were $<$0.5, and 39% of ratios were $>$0.5, which showed a petrogenic origin and coal, gross, and wood combustion origins.

3.4.2. *Principal component analysis (PCA)*

Principal component analysis (PCA) is a statistical tool traditionally used to highlight similarities and differences between large data sets and facilitate better visualization (Simpson et al., 1996; Doong and Lin, 2004). In this study, the PCA analysis was conducted for the sediment samples only. No PCA analysis for the data generated from the analysis of surface water samples was conducted since most PAHs concentrations in the surface water sample were below the method detection limit. The three principal components (PCs-PC1, PC2, and PC3) were extracted in sediment samples that accounted for more than 40% of the total variance. The final coefficients of the eigenvectors based on the PCs were used for drawing inferences about the potential PAHs sources in sediments (Table 4). The PCA biplot of the sediments shown in Fig. 5, described the load of the PAHs at PC-1 and PC-2.

The principal component 1(PC-1) explained 17.58% of the total variance and heavily loaded with the LMW PAHs (NA, AC, ACY), HMW PAHs (BkF, IN, BgP), and moderately loaded with PAHs (Flur, BaA, Chry, BbF, BaP, DA). The PAH NA is the main component of diesel fuels and gasoline, which may be formed by incomplete combustion (Dong and Lee 2009; Soltani et al., 2015). PAHs such as BkF are potentially resulting from wood combustion sources (Bixiong et al., 2006), and IN may be originated from pyrolysis or incomplete fuel combustion (Jiang et al., 2009). BgP is generally a marker of automobile emissions (Liu et al., 2009b). Thus, PC-1 describes PAHs' sources due to incomplete fuel combustion and wood burning. The diagnostic ratios analysis also validated similar results. The principal component- 2(PC-2) and principal component- 3 (PC-3) analysis explained 11.72% and (11.35%) of the total variance and heavily loaded with the PAHs, such as AC in PC-2 and the PAHs Fluor, Flur, Chry, BbF, and DA were heavily loaded in both PC-1 and PC-2. The PAH Chry was predominant in most sediment samples and generally identified with the coal combustion (Tavakoly et al., 2014). The DRB is one of the predominant mining and industrialized area in Jharkhand and West Bengal. It has some of the largest coalfields such as Jharia coalfield, North Kanakpura coalfield, East Bokaro coalfield, and Raniganj coalfield located within the DRB. As such, coal combustion is one of the significant sources of emission of PAHs in the DRB. Other PAHs like Flur and DA are primarily originated from the high amount of vehicular emissions (Tavakoly et al., 2014). Transportation of coal from mining sites may be a significant reason for vehicular emissions. From PCA and diagnostic ratio, it is evident that PAHs in the DRB primarily originate from coal and fuel combustion, petrogenic, and pyrolysis sources.

3.5. *Potential ecosystem risk assessment*

The PAHs concentration in surface water samples at the DRB was less than 10 μg/L, except for two PAHs ACY (36 μg/L) and BaA (23 μg/L). These concentrations were higher than the World Health Organization stipulated 50 ng/L standards for surface and coastal waters (WHO, 1998). According to one estimate, PAHs' aqueous concentration greater than 10 μg/L suggests extensive water contamination by PAHs (Chen et al., 2004). The higher concentration of these PAHs potentially results in adverse biological effects for the aquatic organisms. Environmental scientists have developed effect-based guideline values on the relationship between the contaminant concentration and toxic response exhibited by an organism. These values were used to estimate the amount of pollution in sediments (McCready et al., 2006; Liu et al., 2009a, 2014; Long et al., 1995; Wang et al., 2017). The effects were characterized as the effect range-low (ER-L) and effect range-median (ER-M) (Table 5). The probability of negative toxic effect is more than 50%, and lower than 10% suggested that PAHs' concentration in sediments is higher than ER-M and lower than ER-L values. The concentration of individual PAHs recorded in this study ranged from non-detect (ND) to 582 ng/g. All 16 PAHs concentration was less than the ER-M values, while the PAHs like AC, ACY, Fluor, BaA, and Chry have higher concentration values than the ER-L. Hence these PAHs can exert adverse biological responses at the sampling sites within the DRB. Uncertainties are ubiquitous in all-natural and life sciences (Mudelsee et al., 2019); therefore, validation of results with a higher confidence interval is required. The uncertainties from the measurements arise due to limited data size; hence the estimation may not be actual. So, an uncertainty measure must accompany estimation results. By this, the assessment of the accuracy of the estimation of results will be allowed. Hence it needs to present the estimates with the error.

3.6. *Human health risk assessment*

Human health risks due to exposure to the aqueous and sediment-bound PAHs were assessed. The ILCR were calculated for exposure to PAHs to children and adults. The results show that the ILCR for seven carcinogenic PAHs in surface water samples of the DRB ranged from ND to 4.25×10^{-5} for children and ND to 7.21×10^{-5} for adults. The RI (sum of ILCR) for the seven carcinogenic PAHs was 4.3×10^{-5} for children and 7.3×10^{-5} for adults (Table 6), respectively. According to the regulatory guidelines, ILCR $\leq 10^{-6}$, indicates no or negligible risk similar to the risk arising from exposure to therapeutic procedures like X-ray. When ILCR$> 10^{-4}$ indicates a high risk with adverse health effects like cancer. Between these two extreme ILCR, the risk is considered

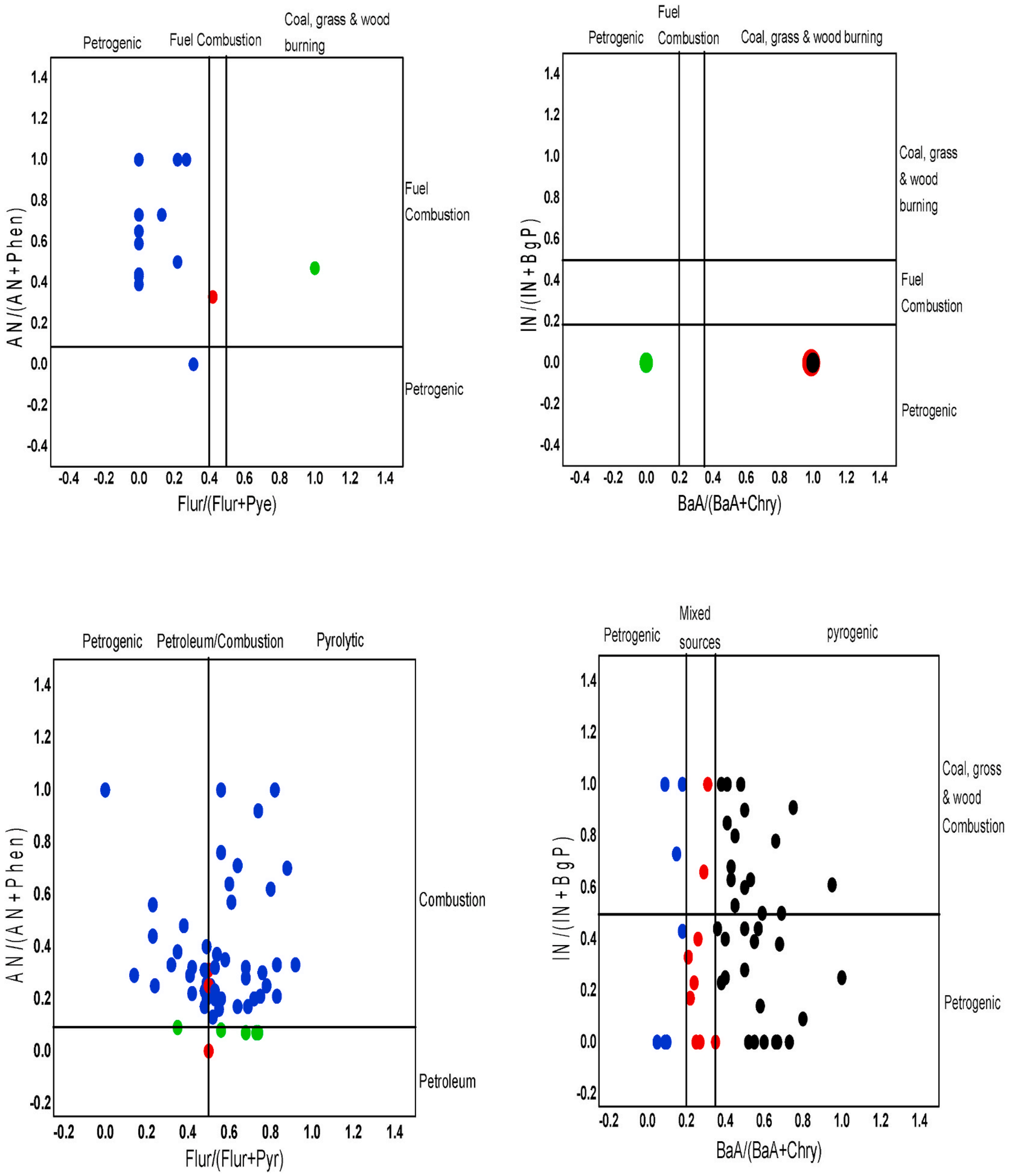


Fig. 4. Diagnostic ratios of surface water and sediments of Damodar Basin.

acceptable (Huang et al., 2016; Liu et al., 2017). The ILCRs calculated in this study are within the acceptable limit. Other carcinogenic PAHs like BaP, DA, and IN had concentration below the method detection limit, and hence no ILCR was calculated.

The TEQ and MEQ values for the carcinogenic PAHs (BaA, Chry, BbF, BkF, BaP, DA, BgP, IN) in the sediments were calculated using the values of TEF and MEF (Table 6). The total TEQ and MEQ values for eight PAHs in sediments were 1865 ng/kg and 1665 ng/kg. Higher TEQ and MEQ values were due to the observed higher concentrations of BaA, BbF, BaP, and DA. Their higher concentration accounted for 92% of the total TEQ values and 79% of the total MEQ values. For other carcinogenic PAHs, TEQ and MEQ values were significantly less except for BgP in MEQ that accounts for 8% of the total values.

4. Conclusion

In this study, we investigated the occurrence and distribution of USEPA regulated 16 PAHs in the DRB and documented its concentration levels, contamination sources, human health, and ecological risk assessment. Surprisingly, some high molecular weight PAHs (BaP, DA, and IN) were absent in the surface water samples, while others were detected at low concentration. On the contrary, much higher concentrations of the low molecular weight PAHs (PAH-ACY and PAH-BaA) were detected in the surface water samples. The diagnostic ratios analysis suggests that PAHs in the surface water samples were attributed to the petrogenic origin and fuel combustion. The concentration of some PAHs in the sediment samples were below the effect range median (ER-M) values, while the concentration of some PAHs like AC, ACY, Fluor, BaA, and Chry were above effect range low (ER-L) values, indicating potential adverse ecological risk. Two sampling sites S30 and S36 had a higher concentration of ACY and BaA, respectively. Due to their low concentration in surface water, the ILCR was below the acceptable level indicating no carcinogenic risk to human health. The concentration of some PAHs such as ACY and BaA in surface water were above the threshold limit of 10 μg/L, indicating an adverse effect on aquatic organisms. The high amount of coal mining and industrial emission in this

Table 4
The extracted principal components (PC-1, PC-2 and PC-3) analysis of sediments samples.

PAHs	PC-1(17.58%)	PC-2(11.72%)	PC-3(11.35%)
NA	0.343	−0.276	0.019
AC	0.326	0.352	−0.172
ACY	0.32	0.166	−0.25
Fluor	0.006	0.298	0.33
Phen	0.124	0.196	−0.417
AN	0.157	−0.422	0.044
Flur	0.213	0.206	0.353
Pye	0.07	−0.104	−0.251
BaA	0.217	0.018	−0.241
Chry	0.216	0.212	0.32
BbF	0.264	0.228	0.141
BkF	0.313	−0.351	0.201
BaP	0.253	−0.122	0.015
DA	0.217	0.267	0.213
IN	0.313	−0.322	0.203
BgP	0.33	0.011	−0.352

area may cause PAHs contamination in sediments. The diagnostic ratios and PCA analysis suggest that the PAHs' occurrence in sediments were originated from coal and fuel combustion, petrogenic, and pyrolysis sources. Higher values of ER-L and ER-M were recorded for PAHs in the sediment samples. These higher values are attributed to the widespread detection of 4-ring PAHs, with some sampling sites at Barakar River of the DRB that had mean concentration as high as 83 ng/g (Chry). The total TEQ and MEQ values for sediment samples were calculated as 1865 ng/kg and 1665 ng/kg, which are significantly higher than the values reported by other researchers.

The DRB is located in one of the major coal mining areas accounting for nearly 46% of all Indian coal reserves. For example, the Rajrappa coal mining area, situated on the bank of the Damodar River, holds a coal reserve of 72 million tons alone (Mohanty et al., 2018). Surface water and groundwater in the DRB are at increased risk of pollution due to poorly managed mining waste. Discharge of a large volume of polluted water from underground/open cast mines into the adjoining area is a significant concern in DRB. Groundwater in the DRB, especially in the Jharia coalfield (one of the four large coalfields located in the DRB), occurs mostly in the unconfined shallow aquifers where pre-monsoon groundwater depth ranges from 3 to 5 m (Singh et al., 2008). Discharge of drilling waste, especially from the opencast mining activities, dramatically increases groundwater pollution chances. Activities such as coal washing, improper management of liquid effluent generated during the mining operation (opencast mines), unregulated discharge of slurry, and surface runoff have great potential to contaminate the water resources in the area. Water pollution by acid mine drainage is a serious environmental concern worldwide; luckily, this is

Table 5
The standard toxicity guideline values (ng/g) of 16 PAHs in sediments.

PAHs	ER-L	ER-M
NA	160	2100
AC	16	500
ACY	44	640
Fluor	19	540
Phen	240	1500
AN	85.3	1100
Flur	600	5100
Pye	665	2600
BaA	261	1600
Chry	384	2800
BbF	320	1800
BkF	280	1620
BaP	430	1600
DA	63.4	260
BgP	85	1600
IN	240	–

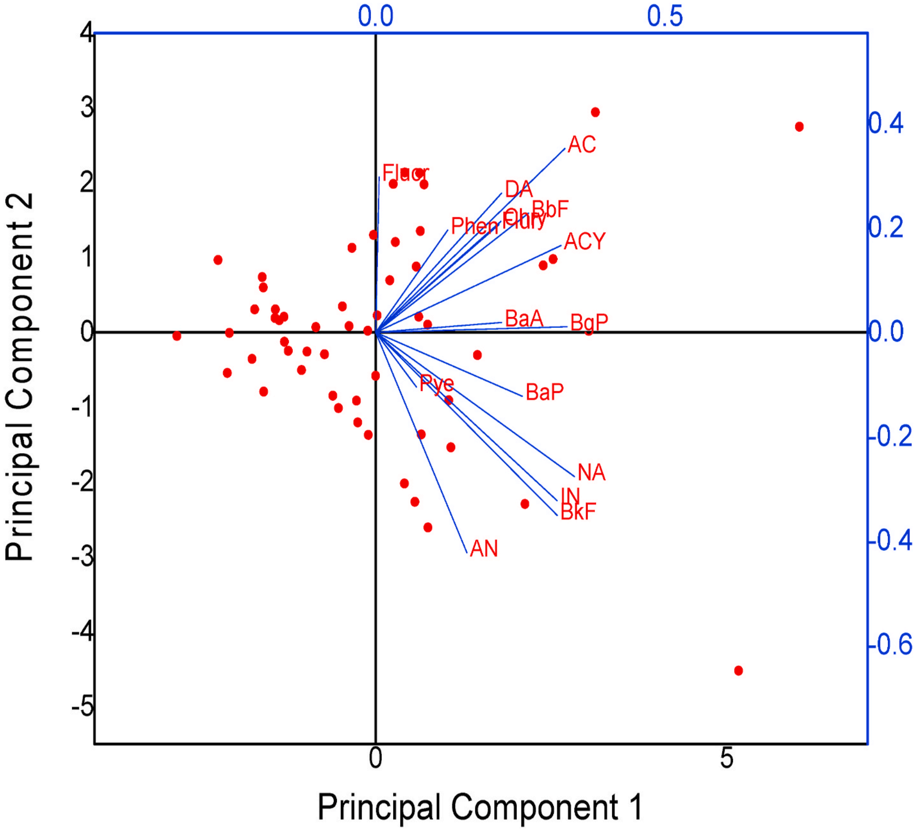


Fig. 5. The PCA biplot showing loads on PC-1 and PC-2 in sediments of Damodar basin.

Table 6
ILCR and RI of carcinogenic PAHs in surface water samples and TEQ and MEQ values of Damodar basin.

Carcinogenic PAHs	CSF	TEF	MEF	KP	ILCR		Σ C_n.TEF_n	Σ C_n. MEF_n
					Child	Adult		
BaA	0.73	0.1	0.082	8.10×10^{-1}	4.25×10^{-5}	7.21×10^{-5}	281	230
Chry	0.073	0.01	0.017	8.10×10^{-1}	0.003×10^{-5}	0.005×10^{-5}	45	77
BbF	0.73	0.1	0.25	1.2	0.04×10^{-5}	0.07×10^{-7}	146	365
BkF	0.73	0.1	0.11	–	–	–	40	44
BaP	7.3	1	1	1.2	ND	ND	493	493
DA	7.3	1	0.29	2.7	ND	ND	812	235
IN	0.73	0.01	0.19	1.9	ND	ND	4	84
BgP	–	0.1	0.31	–	–	–	43	135
RI = Σ ILCR					4.3×10^{-5}	7.3×10^{-5}		
Total TEQ and MEQ							1865	1665

(Wang et al., 2009a,b; CCME 2010; Kumar et al., 2015; Adeniji et al., 2019; Benson et al., 2017; Adeniji et al., 2019a).

not a significant problem in the DRB due to low sulfur and pyrite content coal in this region (Tiwary and Dhar, 1994).

Given that, Damodar River is the central part of the basin, and millions of people living in the adjoining area use DRB water for drinking and agricultural purposes, preserving the water quality in the DRB area should be given priority. Proactive measures are required to mitigate the continued deterioration of water quality in the DRB. Particular emphasis should be placed on better management of mine waste and implementing best management practices for controlling sub-surface runoff originating from the mining areas.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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