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Source apportionment of heavy metals and their ecological risk in a tropical river basin system

Balwant Kumar[1] · Umesh Kumar Singh[1] (ID)

Abstract

Surface water and sediment samples were collected from Ajay River basin to appraise the behavior of heavy metals with surrounding environments and their inter-elemental relationships. Parameters like pH and organic carbon are having a minimal role in heavy metal distribution while some elements like Fe and Cu showed great affinity for organic matter based on linear regression analysis (LRA). Ficklin diagram justified that river basin is not contaminated through acidic pollutants. The river basin is highly enriched with Cu, Cd, Pb, and Ni which were much higher than world average values, average shale standard, effect range low (ERL), and threshold effect level (TEL). PCA and LRA verified that Cu, Cd, Pb, and Ni were mainly derived from anthropogenic inputs, and others like Fe, Mn, Zn, and Co came from geogenic sources. Pollution indices revealed that river basin is moderately to highly contaminated by Cu, Cd, and Ni. Furthermore, Ajay River basin is under strong potential ecological risk based on the obtained value of risk index and probable effect level/effect range median quotient index. However, river basin is strongly influenced by lithological properties, diversified hydrogeological settings, mineralization and mobilization of subsurface materials, and urban and industrial effluents which are controlling the heavy metals.

Keywords Heavy metals · Ecological risk index · Water/sediment pollution · Geochemistry · Ajay River basin

Introduction

Heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), nickel (Ni), and zinc (Zn) are persistent contaminants within the aquatic environment and have the potential to elicit toxic effects at elevated concentration (Torri and Correa 2012; Atibu et al. 2016; Castro-Catala et al. 2016; Antunes et al. 2018). River basins are highly susceptible for variety of contaminants including accumulation of heavy metals and metalloids due to their openness which allows to the disposal of metal-containing waste from mining, industries, and atmospheric deposition (Martinez-Santos et al.

2015). Metal contaminations in natural waters and sediments have gained much attention due to their abundance, persistence, and potential to induce toxic effects (Cakmak et al. 2017; Milacic et al. 2017). In general, river sediment is considered as basic environmental components, but they also serve as sinks for metals (Islam et al. 2015). Heavy metals in the environment are generally derived from two sources such as anthropogenic sources, which are directly linked with human activity, and natural circulation of the metals through rock weathering, mineralization, dust storm, and volcanic eruption (Jha et al. 2009; Siudek et al. 2015). The composition of river waters and sediment is diverse, varying with factors such as climatic condition, hydrogeological setting, and anthropogenic activity (Kumar et al. 2017; Wang and Wang 2017). In the last few years, a great deal of concern has been expressed over the problems of river basin contamination related to heavy metal pollution (Adamu et al. 2015; Ali et al. 2016; Ma et al. 2016; Zhang et al. 2016; Strady et al. 2017). Unfortunately, large quantities of heavy metals have been released into the rivers due to rapid urbanization and change in land use pattern as well as the expansion of industrial and agricultural sectors (Islam et al. 2015). Consequently, river received a large amount of partially treated and untreated

✉ Umesh Kumar Singh
umeshkumar.singh@visva-bharati.ac.in; umeshjnu@gmail.com

[1] Integrated Science Education and Research Centre (ISERC), Institute of Science, Visva-Bharati, Santiniketan, Birbhum, West Bengal 731235, India

wastewater from urban and industrial centers which has led to increased level of metals in the river (Sharma et al. 2017). The heavy metals can bioaccumulate in the animals and plants as well as making their way to humans through the food chain (Ungureanu et al. 2016). In developing country like India, most parts of the developmental activities depend on the rivers for disposal of various anthropogenic waste associated with toxic chemicals, biodegradable waste, and ionized substances (Kumar et al. 2015). It is interesting to note that about 70% of the available surface water is polluted mainly due to the discharge of untreated sewage (Joshi et al. 2009; Kumar et al. 2014). Therefore, these uncertainties may increase the contamination in the river basin and change the natural composition of water and sediment, which can lead to high risk for human population (Kumar et al. 2016).

However, pollution by heavy metals such as Pb, Cd, Ni, Cu, and Co in freshwater is considered potentially hazardous to human health and deems to be undesirable (Vu et al. 2017). The exposure of human population for these metals adversely affects the various organs such as the kidney, gastrointestinal tract, and nervous system as well as disrupts the transport activities of phosphate biocompounds (Lohani et al. 2008; Jaishankar et al. 2014; Singh and Kalamdhad 2018). Some essential elements like Fe, Mn, and Zn are also harmful to human health especially when they are above the desirable limit set by different national and international regulatory bodies (Prashanth et al. 2015). Various researchers have concluded that many surface waters are strongly affected by high concentration of heavy metals due to excess inputs of undesirable anthropogenic substances, which produce various types of contamination and poses environmental risk for the aquatic environment (Ciszewski et al. 2013; Liu et al. 2013; Candeias et al. 2014; Qasim and Motelica-Heino 2014; Adamu et al. 2015; Siudek et al. 2015; Pandey et al. 2016). Accumulations of heavy metals in the aquatic system pose a high ecological risk and are responsible for high mortality rate, alteration in growth, impair reproduction, and loss of species diversity (Devanesan et al. 2017; Mohamaden et al. 2017). However, the mobility of heavy metals in the river depends on various factors such as hydrogeological settings, mineralogical composition of subsurface materials, and different geochemical process (dissolution and precipitation) as well as climatic condition (Shumilin et al. 2011; Jiang et al. 2013). Therefore, it is important to understand the mechanism of heavy metals and their complexes in the river which controls the composition of river water and sediment (Akcay et al. 2003).

Very few studies have been reported related to fate and transport of heavy metals in Ajay River basin. Singh and Kumar (2017) observed that diverse geological settings, mineralogical composition, and mobility of soil and sediment as well as numerous anthropogenic inputs are major responsible factors for the enhancement of toxic elements in Ajay River

basin. The authors suggested that the water quality of Ajay River basin is unsuitable for drinking and bathing purposes due to high loads of Cd, Pb, and Cu. However, similar studies have been conducted by various researchers worldwide regarding the potential risk of heavy metals to the river ecology and human health. Previous studies confirmed that the heavy metals like As and Cd pose moderate to considerable high ecological risk for the Yangtze River system, China (Wu et al. 2009; Yi et al. 2011). Similar studies conducted by Buschmann et al. (2008) in the Mekong Delta floodplains, Vietnam; Maanan et al. (2014) in Nador lagoon, Morocco; Neyestani et al. (2016) in northern Persian Gulf; and Singh et al. (2018) in East Singhbhum, India, suggest that heavy metals pose moderate to considerable ecological risk and have potentially adverse effects on local residents. However, the present study is focused on how the surface water and sediment properties affect heavy metal enrichment in Ajay River basin. Moreover, the objectives of this study are (a) to evaluate the geochemical properties and enrichment of heavy metals in sediment and surface water, (b) to identify the compositional groups, critical parameters, and geochemical processes which are involved in Ajay River basin, and (c) to evaluate the spatial variation of heavy metals in sediment and surface water to find out their trends and possible sources.

Materials and methods

Study area

Ajay River is situated between "23° 27′ 342″ to "24° 27′ 763″ N latitude and "86° 38′ 156″ to "88° 07′ 729″ E longitudes and spread over 6000 km^2 in three states of India such as Bihar, Jharkhand, and West Bengal (Fig. 1). It originates from the Chakai hill near the Chota Nagpur Plateau and drains densely in populated urban and industrial region of Jharkhand and West Bengal, and lastly, merges into Bhagirathi River at Katwa, West Bengal. Due to the high demand of water for different purposes such as domestic (26.92 million m^3), irrigation (3561.04 million m^3), and industrial uses (1.63 million m^3), river water is trapped from several locations like Jamtara, Chittaranjan, Raniganj, and Andal (Sharma and Chattopadhyay 1998). Several large industries include thermal power plants, fertilizer plants, locomotive industries, coal washeries, and other manufacturing companies of glass, ceramic, and copper cable are settled in the proximity of river basin area. In addition, small industries like manufacturing of copper bucket by villagers and rice and brick industries are also settled in the nearness of river basin. Furthermore, land use pattern of the Ajay basin is characterized into seven categories: agriculture (15.92%), non-agricultural area (13.87%), forest cover (12.22%), land under miscellaneous tree (6.15%), barren land (9.72%), other fallow (9.34%), and current fallow
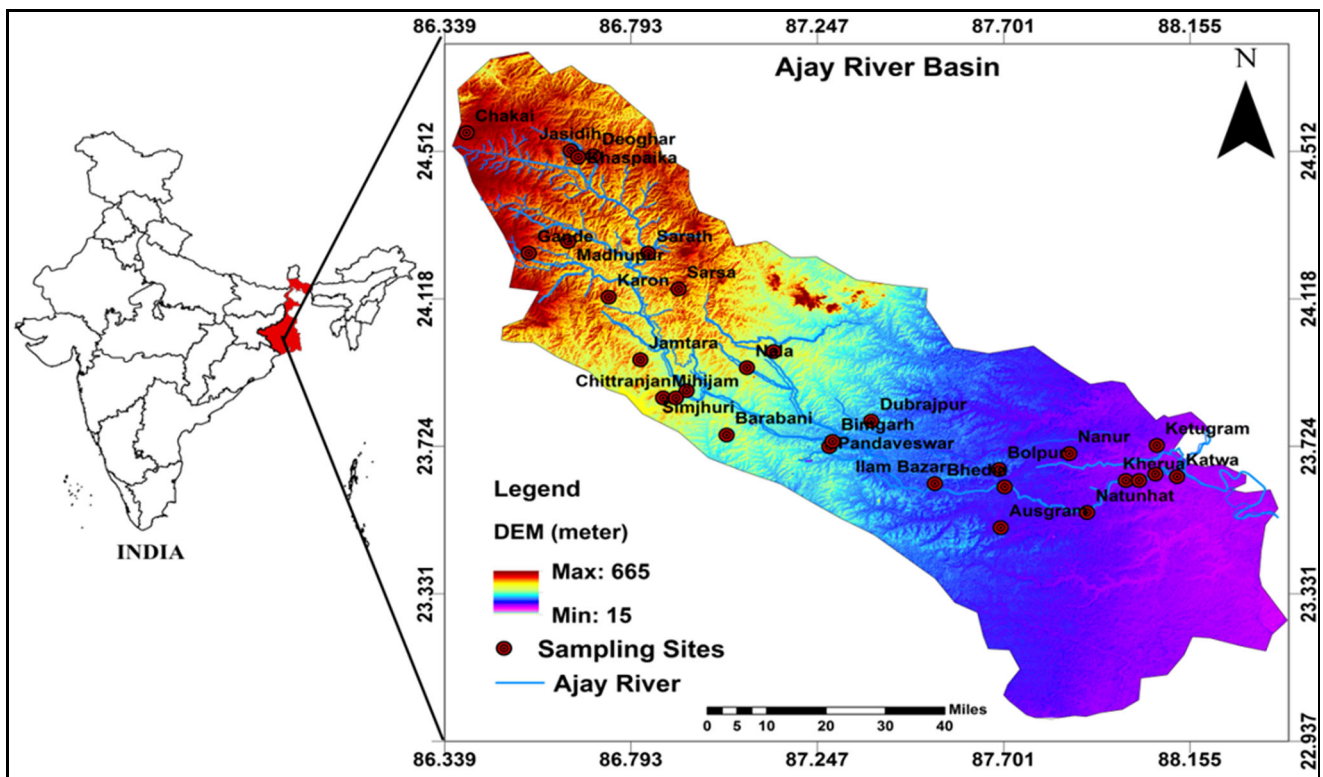
Fig. 1 Description of the study area and sampling sites

(30.83%), respectively (NIH 1999). The study area experiences moderate climatic condition with winter, hot humid summer, and prolonged rainy season (Gupta et al. 2008). The average annual precipitation in the Ajay basin varies from 1280 to 1380 mm (Roy 2012). The lithology of the study area is generally characterized into three groups such as alluvial and major red and yellow loam sedimentary types.

The Ajay River basin is geologically characterized into three major geological setups (Fig. 2, supplementary information) such as Archaean gneissic, Gondwana sedimentary, and Upper Tertiary with a small patch of Quaternary-age rocks. The upper basin lies within Archaean gneissic which is composed of biotite, hornblende, pyroxene granulites, basic intrusive, pegmatite, and quartzite (Ghosh and Guchhait 2015). The middle part of the river encounters Gondwana sedimentary which cover around 8.81% of the total basin area and contains various rock-forming minerals such as biotite, hornblende, pyroxene granulites, basic intrusive, pegmatite, quartzite, and pyrite. The rest of the lower basin is entirely covered with a broad coated alluvial soil over the Tertiary with a small patch of Quaternary-age rocks (Saha and Naskar 2002).

Sampling and analytical procedure

In this study, 60 water and sediment samples from the study area were collected during tow season such as pre-monsoon

(PM) and post-monsoon (POM) from 30 different locations. For the sampling, 1-L sterilized polyethylene bottles for water and cleaned polyethylene bags for sediment were used and transferred to a laboratory as per American Public Health Association (APHA 2005) and the US Environmental Protection Agency (USEPA 1992) guidelines. Millipore water was used for the preparation of all analytical grade reagents and calibration standards. Prior to analyses, all collected samples were digested using nitric acid to remove the interference like organic matter. Acid digestion for water and sediment samples has been carried out separately. For the estimation of dissolved metals, all water samples were filtered using 0.45-μm pore size filter paper. Furthermore, 100 mL filtered water samples were digested using 20 mL 1:1 nitric acid. Similarly, 1 g of air-dried sediment sample was digested with a mixture of concentrated HF, HNO_3, and $HClO_4$ as suggested by Gao et al. (2010) with some modifications. The sediment samples were digested with concentrated 10 mL HF, 4 mL HNO_3, and 2 mL $HClO_4$ in 5:2:1 ratio using the pressure bomb system made up of polytetrafluoroethylene (PTFE) digestion vessels. Further, digested samples were evaporated using 1 mL $HClO_4$ until the appearance of white fumes. After complete cooling, the digested solution was dissolved in 12 N HCl up to 25 ml and filtered with ashless 100 mm (42) Whatman filter. The prepared samples were ten times diluted with Millipore distilled water (Synergy Water Purification System, with a resistivity of 18.2 MΩ cm^{-1} at 25 °C with

150 TOC ≤ 5 ppb) for the analysis. However, instrument calibration with standards, analysis of reagent blanks, and analysis of duplicate samples were performed to check the reproducibility of instruments and quality assurance purposes. The variations of results were consistent with the reference values and less than 5% of the mean. Parameters of both water and sediment like Fe, Mn, Cu, Zn, Pb, Ni, Cd, and Co were estimated through differential pulse anodic stripping voltammeter (DPASV) with standard addition techniques by Metrohm 797 VA Computrace (version 1.3.2.85, serial no. 22179). Ion-selective electrode (ISE-Thermo Scientific) was used for estimation of pH while organic carbon (OC) and organic matter (OM) was assessed through titrimetric method. To evaluate the accuracy and precision value of the analyzed data, spike samples and blanks have been carried out which ensure that environmental samples have not been changed in the matrix. In this study, citified reference materials (CRMs) of Fe (HC894725; 999 ± 2 mg/L), Mn (HC888090; 1001 ± 2 mg/L), Zn (HC766916; 1001 ± 2 mg/L), Pb (HC781141; 999 ± 2 mg/L), Cu (HC784121; 999 ± 2 mg/L), Cd (HC784320; 999 ± 2 mg/L), Ni (HC802075; 999 ± 2 mg/L), and Co (HC895086; 999 ± 2 mg/L) were purchased from Merk India approved by NIST. The results of each metal CRM were between 90 and 105% recovery with ± 5% SD which indicated that the accuracy and reproducibility of the analytical procedure were good.

GIS and statistical analysis

For the grid-based contour map, geological map, and expression of spatial distribution of parameters, ArcGIS-10.3 software developed by ESRI was employed. It was applied according to geographical system coordinates of the study area and their measured data. This software is also applied to estimate the distribution pattern of selected parameters along the sampling sites using inverse distance weighted (IDW) algorithm interpolation method. The Statistical Package for Social Science (IBM-SPSS) V. (20) software was applied to normalize the multifaceted data for the application of multivariate techniques and further statistical analysis. Principle component analysis (PCA) and linear regression analysis (LRA) were carried out in this study to evaluate the possible sources of heavy metals and their compositional relationship. Furthermore, one-way ANOVA test for variables was applied to check the spatial difference in variance at 0.05 significant level using Smirnov and Levene's test.

Assessment of water and sediment contamination through indices approach

In the last few years, much attention has been paid to applying of geochemical and water quality indices based on arithmetic calculation to evaluate the water and sediment characteristics in rating scale (Wang et al. 2014; Herojeet et al. 2015; Islam et al. 2015; Pandey et al. 2015). In this study, to evaluate the degree of contamination and ecological risk by heavy metals, various scientific indices have been carried out, which the details are given below:

Heavy metal pollution index

Heavy metal pollution index (HPI) was calculated based on the assigned weightage (Wi) and recommended standard (Si) for each element to evaluate whether water quality is under critical level (< 100) or above the critical level (> 100) using the following equation given by Horton (1965):

$$HPI = \frac{\sum_{i-1}^{n} W_i Q_i}{\sum_{i-1}^{n} W_i}; Q_i = \sum_{i-1}^{n} \frac{(M_i - I_i)}{(S_i - I_i)} \times 100 \tag{1}$$

W_i = unit weightage for each parameter proposed by Horton (1965); Q_i = sub-index of the ith parameter; M_i is the average concentration of particular examined heavy metal; S_i = permissible limit; and I_i = desirable limits prescribed by Bureau of Indian Standard (BIS 2003), respectively (Prasad and Bose 2001).

Pollution index

Pollution index (PI) was used to characterize each element into groups. PI is combined arithmetic calculation between analyzed metal values and maximum and minimum desirable limits of each metal as prescribed by international and national regulatory standard (Caeiro et al. 2005). The calculation for PI has been done according to the following equation:

$$PI = \frac{\left[\left(\frac{C_i}{S_i} \right) \max + \left(\frac{C_i}{S_i} \right) \min \right]}{2} \tag{2}$$

where Ci is the concentration of each metal; Si (max) is the maximum and S_i (min) is the minimum desirable limits according to national water quality standard. PI value can be subdivided into five classes based on the obtained result such as < 1 = no effect, 1 to 2 = slightly affected, 2 to 3 = moderately affected, 3 to 5 = strongly affected, and > 5 = seriously affected (Caeiro et al. 2005).

Enrichment factor

Enrichment factor (EF) was applied to determine the degree of contamination in sediment samples and to understand the sources of heavy metals for anthropogenic or geogenic origin. In this study, Fe was chosen as a tracer to signify the origin of heavy metals because it significantly affects the behavior of

metals in the aquatic environment. Arithmetic calculation for EF has been done based on the following formula (Grygar et al. 2014):

$$EF = \frac{(C_x/Fe)sample}{(C_x/Fe)background} \qquad (3)$$

where C_x = total metal concentration of each metal; Fe (sample) = sample value of Fe; and Fe (background) = average shale standard. The obtained EF value can be classified into five classes such as < 1 = deficient to minimal, 1–5 = moderate enrichment, 5–20 = significant, 20–40 = very high, and > 40 = extremely high (Sakan et al. 2015).

Geoaccumulation index

Geoaccumulation index (Igeo) was proposed by Muller (1979) to determine the metal accumulation and contamination level in sediments. Igeo values can be obtained using following formula:

$$I_{Geo} = \log_2 \frac{C_n}{1.5 \times B_n} \qquad (4)$$

where C_n is the heavy metal concentration determined in the sediment, B_n is the background heavy metal concentration, and 1.5 is the correction factor for metal lithologic variations (Nethaji et al. 2016). Seven rating scales such as < 0 = unpolluted, < 1 = unpolluted to moderately polluted, < 2 = moderately polluted, < 3 = moderately to highly polluted, < 4 = highly polluted, < 5 = highly to extremely polluted, and ≥ 5 = extremely polluted (Ghrefat and Yusuf 2006).

Probable effect level/effect range median quotient index

Probable effect level (PEL)/effect range median (ERM) quotient index is a unique method to determine the possible biological effect of various potential toxic elements in sediments (Soliman et al. 2015). The values of PEL and ERM for each metal have been listed in Table 1 which was proposed by Long et al. (1995) and Smith et al. (1996), respectively. The arithmetic calculation of mean quotients for heavy metals has been computed using the following equation:

$$PEL/ERM = \sum[C_i/(ERM \text{ or } PEL)]/n \qquad (5)$$

where C_i is the concentration of element. ERM and PEL are the guideline values for the element, and n is the number of metals. In addition, PEL/ERM quotient index value can be categorized into four classes such as < 0.1 = non-toxic, 0.1–0.5 = slightly toxic, 0.5–1.5 = medium toxic, and > 1.5 = highly toxic (Soliman et al. 2015).

Ecological risk index

Ecological risk index (RI) was proposed by Hakanson (1980) to determine the degree of heavy metal pollution in sediment based on toxicity and persistent level and their responses in the environment using the following formula (Tian et al. 2017):

$$RI = \sum_{i=1}^{n} E_r^i \qquad (6)$$

$$E_r^i = T_r^i \times CF \qquad (7)$$

$$CF = \frac{C_o}{C_b} \qquad (8)$$

where E_r^i = ecological risk coefficient, CF = contamination factor, and T_i^r = toxic response factor for Pb (5.0), Cd (30.0), Cu (5.0), Zn (1.0), Ni (5.0), and Mn (1.0). C_o is the observed metal concentration, and C_b is the background value. RI represents four classes based on the obtained values such as RI < 150, low risk; > 150 RI < 300, moderate risk; > 300 RI < 600, high risk; and RI ≥ 600, significantly high risk (Xu et al. 2008).

Results and discussion

The values of heavy metals in 60 water and sediment samples collected from 30 sampling sites of Ajay River basin are shown in Tables 1 and 2 respectively (supplementary information). Descriptive statistics with minimum, maximum, mean, and standard deviation of physicochemical characteristics and elemental concentrations in the water and sediment samples are listed in Table 1.

Physicochemical analysis of water and sediment samples

The availability of heavy metals in sediment and water is highly influenced by a range of pH values of studied samples because it has potential to enhance the mobilization process and increase the solubility of metals in the water (Wang et al. 2015). In this study, the value of pH in water and sediment samples ranged from 6.89 to 7.72 and 7.6 to 8.4 with a mean value of 7.24 ± 0.24 and 8.1 ± 0.2, respectively. Results showed that majority of the samples from the study area are moderately alkaline. The solubility of heavy metals generally depends on the range of pH because it is likely to increase at lower pH and decrease at higher pH values (Rieuwerts et al. 2015). To understand the interrelationship between pH and metals, Ficklin diagram (Ficklin et al. 1992) and linear regression have been employed in this study. Ficklin diagram (Fig. 2a) showed that all the samples are plotted within the neutral or alkaline range with high metals which indicates that river basin is contaminated through the abundance of anthropogenic inputs. However, in the linear regression analysis

Table 1 Statistical description of heavy metals and physicochemical parameters of water and sediment samples with Min (minimum), Max (maximum), SD (standard deviation), ERL (effect range low), ERM (effect range medium), PEL (probable effect level), TEL (threshold effect level), and NG (not given)

Heavy metals in water samples	Unit	Min	Max	Average ± SD	BIS (2003)	WHO (2006)	World average[a]	World average[b]	Analytical range (μg/L to mg/L)
Fe	mg/L	1.03	4.58	2.50 ± 0.97	0.3	0.3	0.67	0.055	0.1–100
Mn	mg/L	0.07	0.84	0.39 ± 0.20	0.1	0.1	0.005	0.006	0.02–100
Cu	mg/L	0.04	0.95	0.14 ± 0.20	0.05	0.05	0.005	0.001	0.01–50
Zn	mg/L	0.34	1.59	0.90 ± 0.33	5	5	0.01	0.01	0.001–100
Ni	mg/L	0.01	0.98	0.06 ± 0.12	0.02	0.07	0.0003	0.0003	0.02–1000
Pb	mg/L	0.02	0.15	0.06 ± 0.03	0.01	0.01	0.0003	0.0002	0.2–50
Cd	mg/L	0.01	0.10	0.04 ± 0.03	0.003	0.003	NG	NG	0.01–10
Co	mg/L	0.01	0.09	0.03 ± 0.02	0.01	0.004	0.0002	0.0002	0.05–100
pH	–	6.89	7.72	7.24 ± 0.24	6.5–8.5	6.5–8.5	NG	NG	0.1–13.9
OC	mg/L	0.003	0.12	0.02 ± 0.02	NG	NG	NG	NG	–
Heavy metals in sediment samples	Unit	Min	Max	Average ± SD	Shale standard[c]	ERL[d]	ERM[d]	PEL[e]	TEL[e]
Fe	mg/kg	31,400	48,900	39,577 ± 4040	47,200	NG	NG	NG	NG
Mn	mg/kg	78	112	95 ± 8.1	850	NG	NG	NG	NG
Cu	mg/kg	49	150	89 ± 23	45	34	270	197	37.3
Zn	mg/kg	42	183	84 ± 26	95	150	410	315	123
Ni	mg/kg	35	94	63 ± 16	68	20.9	51.6	36	18
Pb	mg/kg	5.1	17	11 ± 2.2	20	46.7	208	91.3	35
Cd	mg/kg	1.0	3.1	1.7 ± 0.4	0.3	1.2	9.6	3.53	0.596
Co	mg/kg	5.1	16	10 ± 2.8	19	NG	NG	NG	NG
pH	–	7.6	8.4	8.1 ± 0.2	NG	NG	NG	NG	NG
OC	%	6.9	8.7	7.7 ± 0.4	NG	NG	NG	NG	NG

[a] Bryan (1976)

[b] Salomons and Forstner (1984)

[c] Turekian and Wedepohl (1961)

[d] Long et al. (1995)

[e] Smith et al. (1996)

(Fig. 2)b, pH was not correlated with the majority of the heavy metals except Fe ($P = 0.0001$), Cu ($P = 0.019$), Zn ($P = 0.009$), and Ni ($P = 0.0048$). This is mainly due to the neutral to sub-alkaline environment of the river basin, which makes the limited importance of pH for metal distribution (Ungureanu et al. 2016). However, an alkaline condition also enhanced the precipitation of Fe and is responsible for hydrous oxide coatings on other mineral surfaces that enhance the co-precipitation of metals especially Cu and Mn in the aquatic system (Sipos et al. 2014). Ni is a water-soluble trace metal, and their solubility decreases at higher pH and increases at lower pH values (Mellis et al. 2004).

The surface water and sediment samples of the study area had low organic carbon (OC) and organic matter (OM) contents, respectively. The OC and OM values in the study region vary from 0.003 to 0.12 mg/L and 6.9 to 8.7% with an average value of 0.02 ± 0.02 mg/L and 7.7 ± 0.4%, respectively. A lesser amount of organic content in the river basin reveals minimal retention of heavy metals by organic complexes and soil matrix. However, in the aquatic environment, heavy metals can be associated with different organic complexes such as clay, metal oxides, and organic matter (Shetye et al. 2009). In the regression analysis, the behavior of metals over the OC does not signify the interrelationship between themselves whereas OM shows good correlation with Fe ($P = 0.031$), Mn ($P = 0.048$), Cu ($P = 0.0001$), and Cd ($P = 0.013$) in this region (Fig. 2c). Fe and Mn have shown a relatively high affinity for OM because both these are generally involved in the oxidation process and play a major role in mineralization and photo-oxidation of organic materials (Reader et al. 2014). Furthermore, in the aquatic environment, Cu and Cd are generally associated with organic complexes such as humic and fulvic acids that have high affinity to bind Cu and Cd by the formation of strong organo-metallic complexes
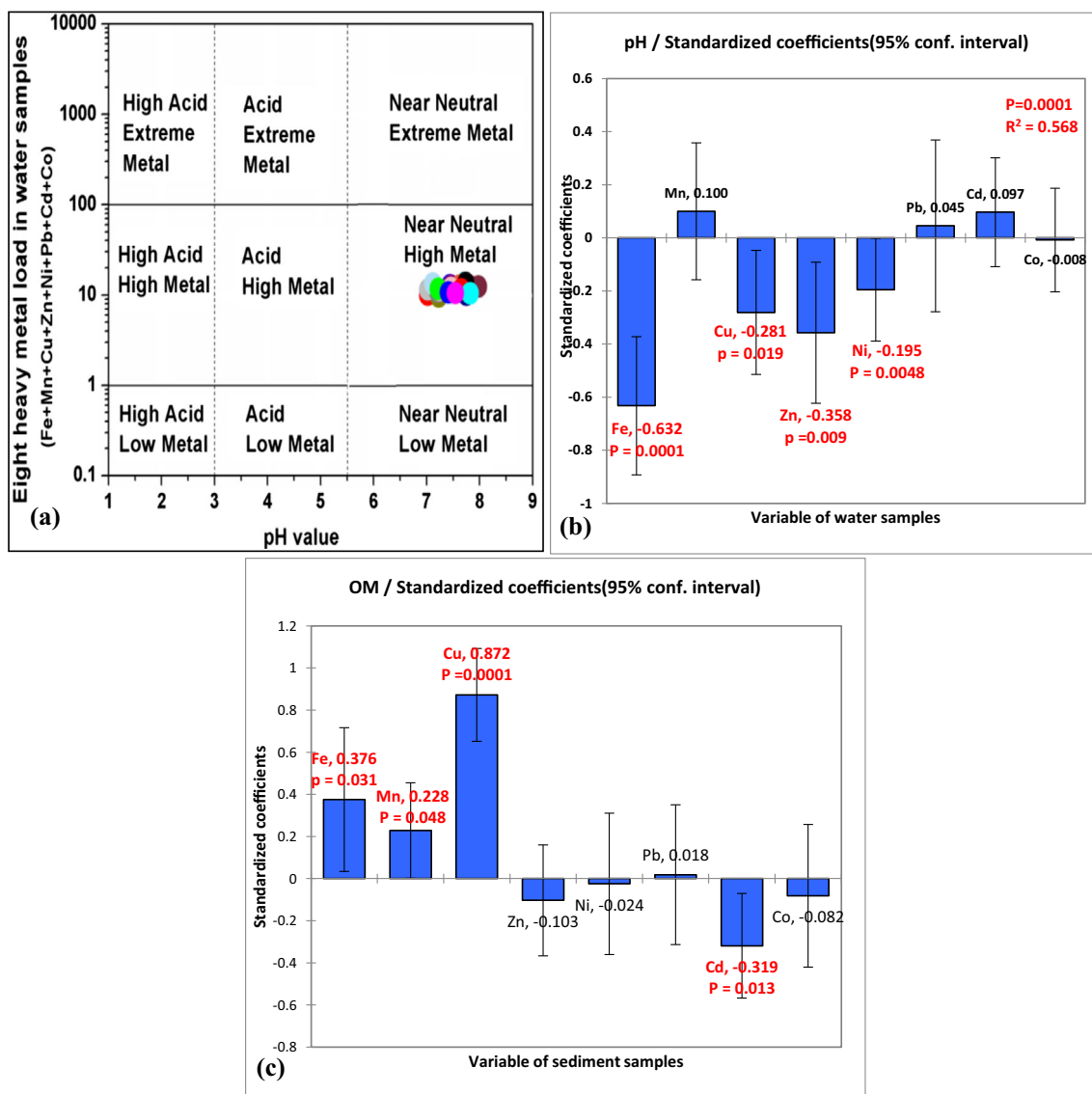
Fig. 2 Ficklin diagram for **a** interrelationship of pH with PTEs load, **b** linear regression analysis of PTEs with pH values, and **c** linear regression analysis of sediments PTEs with OM value

(Rieuwerts et al. 2015). Therefore, such relationship between OM and Cu and Cd might be possible in the river basin which makes a good correlation between them. However, Pb, Co, Ni, and Zn show a poor affinity for organic matter because of higher deposition patterns of the river basin, resulting in minimal retention of these elements by organic complexes (Rajmohan et al. 2014).

Heavy metal distributions in water and sediment samples

In the aquatic environment, sediment serves as a sink of metals because it is possible for the metals to remain in the sediment with numerous organic complexes. However, a significant amount of metals can be released back to the water column

under favorable physicochemical conditions and form a detrimental condition of water quality (Vu et al. 2017). In this study, dissolved metal concentrations were significantly greater than the reported average concentrations for world rivers (Bryan 1976; Salomons and Forstner 1984). Similarly, the majority of the metals like Fe (1.03–4.58 mg/L), Mn (0.07–0.84 mg/L), Cu (0.04–0.95 mg/L), Pb (0.02–0.15 mg/L), Cd (0.01–0.1 mg/L), Ni (0.01–0.98 mg/L), and Co (0.01–0.09 mg/L) concentration are above the permissible limits of drinking water guidelines (Fig. 4, supplementary information) given by the Bureau Indian Standard (BIS 2003) and World Health Organization (WHO 2006). Statistical analysis of variable (ANOVA) at the 0.05 significant level suggests that all sites are significantly different based on the input variables. In this study, all the samples ($n = 60$) have high Fe and Mn concentration. Lithology of the

Ajay basin characterizes with alluvial and lateritic soil terrain which are the important sources of both these elements in this region. In the upper basin, significant loads of industrial and urban effluent and other sub-surface activities like mineral exploration and metal plating industries may also contribute a significant amount of Fe and Mn. Furthermore, the concentration of Cu was high in all the samples as compared to regulatory standard. The higher concentrations of Cu were observed especially in the middle and lower parts of the river basin. Higher concentration of Cu in this region is linked to the anthropogenic source because large numbers of villagers manufacture copper buckets without proper methods and management, which may cause dispersion of Cu from its source and enter into the river basin. In the majority of the samples, Ni and Co were observed very high especially in the middle and lower parts of the river basin. Higher concentration of Ni and Co along both these regions represents a mixture of lithogenic and anthropogenic sources. Generally, both these elements are much more abundant in the lateritic soil which is a common lithogenic source along these sites. In addition, large agriculture intensive area associated with chemical fertilizers and pesticides is also contributing a significant amount of Ni and Co along these sites. Similarly, higher concentrations of Cd and Pb in the study area are considered as of anthropogenic origin because refusal evidence is available from geogenic sources. Therefore, a higher concentration of Pb and Cd in the water could be derived from effluent-carrying drainage of domestic and industrial centers, mining processing machineries, and disposal discarded electronic waste.

Generally, heavy metals are quickly deposited and strongly associated with various sediment materials under favorable condition such as pH, temperature, and resuspension (Vu et al. 2017). Therefore, it is important to evaluate the heavy metal concentrations in the sediment samples. In this study, the concentrations of Fe (31400–48,900 mg/Kg), Mn (78–112 mg/Kg), Pb (5–17 mg/Kg), and Co (5–16 mg/Kg) in the sediment samples were found below the shale standard values. However, the concentration of Cu (49–150 mg/Kg), Ni (35–94 mg/Kg), and Cd (1–3.1 mg/Kg) in all samples were found above the shale standard values (Fig. 5, supplementary information). Similarly, mean concentrations of Cu (89 ± 23 mg/Kg), Ni (63 ± 16 mg/Kg), and Cd (1.7 ± 0.4 mg/Kg) were observed very high as compared to effect range low (ERL) and threshold effect level (TEL) value. The results suggest that Cu, Cd, and Ni are the most widespread sediment contaminants in the Ajay River basin which caused the unfavorable condition for aquatic system. ANOVA at 0.05 significant level suggests that all sites are significantly different based on the input variables. The concentrations of Cu, Cd, and Ni in all samples ($n = 60$) were found significantly high as compared to shale standard, ERL, and TEL value with high standard deviation which indicates the river gets a significant amount of anthropogenic wastes associated with toxic chemicals and various potential toxic elements

from urban and industrial zones. Most of the industrialized zone in the proximity of Ajay River is under Asansol subdivision and Durgapur subdivision which have a series of large and medium industries like Indian Iron and Steel Company at Kulti, Chittaranjan Locomotive at Chittaranjan, Hindustan Cables Ltd. at Rupnarayanpur, and cottage industry at Katwa. Furthermore, various iron as well as copper utensils are made by villagers including gold and silver smithy, lime making, leather work, and oil crushing.

Compositional analysis of heavy metals in water and sediment

Linear regression analysis

Linear regression analysis (LRA) was adopted in this study to determine inter-elemental relationships among different metals in water (Fig. 3a) and sediment samples (Fig. 3b). The nature of heavy metals in the river water and sediment could be effectively explained by regression analysis. To evaluate the inter-elemental relationships, Fe was used as a tracer because it significantly affects the behavior of metals in the aquatic system (Sipos et al. 2014). In this study, Fe has shown good relation with Mn ($P = 0.005$), Zn ($P = 0.005$), Cu ($P = 0.032$), and Pb ($P = 0.0001$) in water samples. Similarly, in the sediment samples, Fe has a strong linear relationship with Cu ($P = 0.0001$), Zn ($P = 0.0001$), and Cd ($P = 0.001$). The strong relation between Fe and Mn signifies the weathering of minerals like ferromagnesian, manganite, and ilmenite in this region. In addition, such relation might be due to the presence of lateritic soil in the study area which is a common lithogenic source of both elements. Furthermore, the remarkable relationship of Cu, Cd, and Pb with Fe signifies the proof of anthropogenic contribution because less evidence of geogenic sources of these elements is available in this area. Partial treated and untreated sewage as well as agricultural wastes are a common source of these contaminants in this area. However, mineral exploration, mining of coal, and gradual development of several small and large-scale industries in the proximity of river basin without proper management plan may also be responsible for the enhancement of thess contaminants in the river basin.

Principle component analysis

To take environmental measures subjected to heavy metal contamination in aquatic system, it is important to evaluate the critical parameters and sources which indicate the variation in sediment and water quality. In this study, principal component analysis (PCA) was also carried out to evaluate important parameters in the whole dataset and their possible sources which will be helpful to reduce insignificant parameters from monitoring stations (Shreshtha and Kazama 2007; Kumar et al. 2018). However, two principal components have been developed for
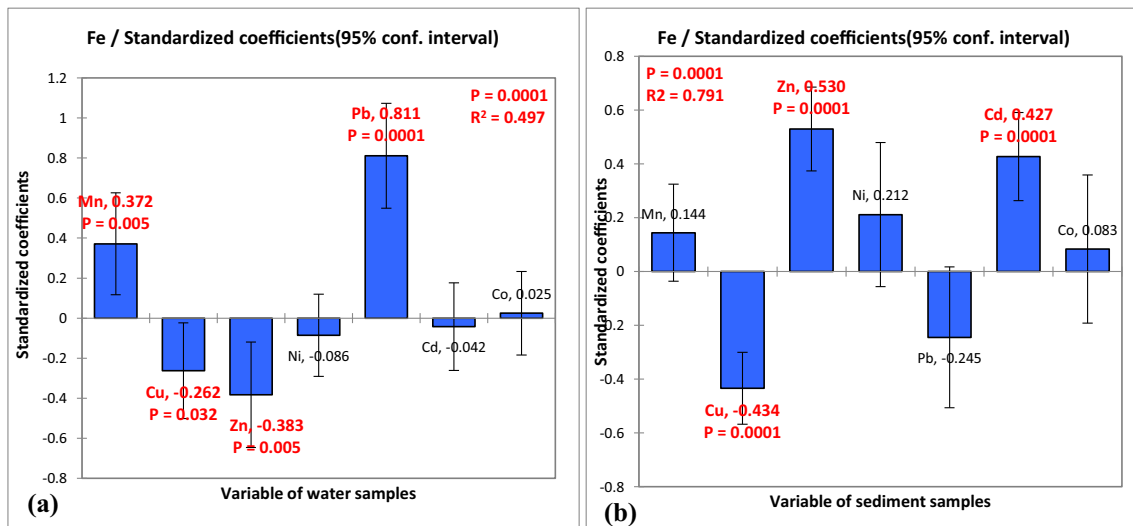
Fig. 3 Linear regression analysis of **a** water's PTEs with Fe value and **b** sediment's PTEs with Fe value

water and sediment samples separately, which explain 45 and 57% of the cumulative variance, respectively.

The first component (D1) for water samples, explains 25% of the total variance (Fig. 4a), contains strong positive loadings of Cu, Zn, and Pb; moderate loading of Ni; and negative loading of Mn. D1 signifies that the water of the basin directly influenced by anthropogenic sources such as urban and industrial effluents as well as agricultural runoff which enhances the concentration of Cu, Zn, Pb, and Ni. In addition, negative loading of Mn in D1 signifies that the lateritic soil which contains significant amount of Mn plays an important role in the availability of this element in the study area. Similarly, D2 explaining 20% of the total variance that dominantly contains Fe and Pb suggests an important role of Fe in the dissolution and distribution of Pb in the river basin. In the aquatic system, the mobility of Pb is

comparatively very low, but it has similar affinity like Fe to the ligands (Dong et al. 2000). Therefore, because of that, both these parameters show similar distribution pattern in the river basin. The negative loading of pH indicated that it has a minimal role in heavy metal distribution in the Ajay River basin.

Furthermore, first principle component (D1) of sediment samples (Fig. 4b) was obtained to explain 36% of the total variance. In the D1, strong positive loadings of Ni, Pb, and Co with moderate loadings of Fe and Mn signify the evidence of anthropogenic influences from paint industries, cement and chemical industries, glass-producing units, and thermal power plants. Similarly, moderate loadings of Fe and Mn in D1 reveal that both these elements are mainly derived from lithogenic origin because weathering of ferromagnesian, manganite, and ilmenite as well as the presence of lateritic terrain is a common
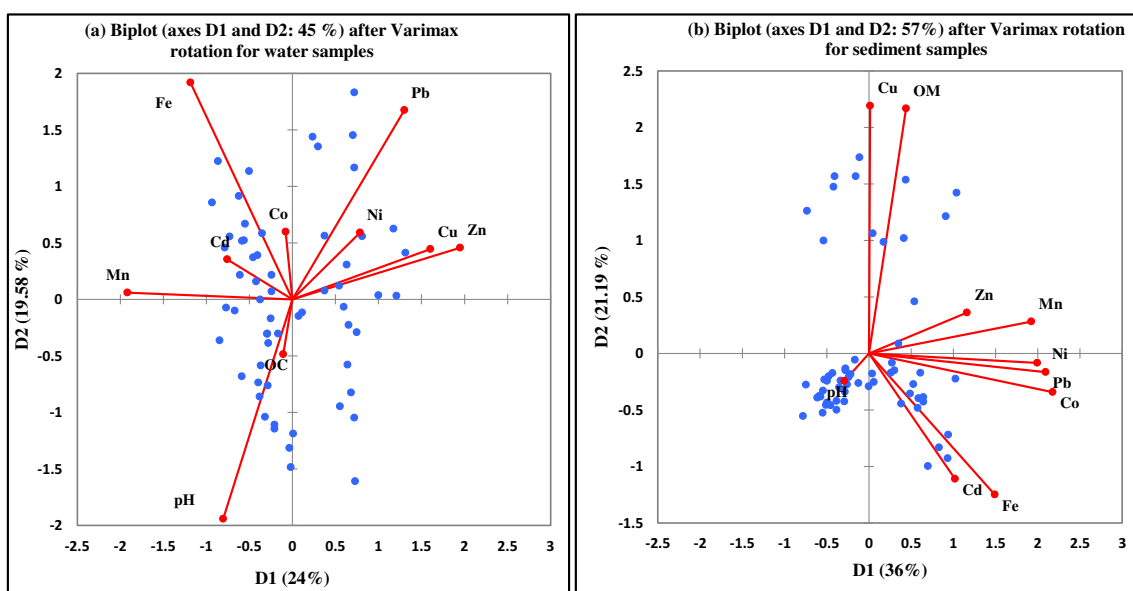

Fig. 4 Biplot of the first two components which explained the **a** 45% of variance for water samples and **b** 57% of variance for sediment sample

source of both elements in this area. Similarly, D2 explains that 21% of the total variance dominantly contains Cu and OM. The result suggests that OM plays an important role in the dissolution and distribution of Cu in the study area. However, OM is an important physicochemical characteristic which plays a major role in the mineralization and mobilization of Cu elements in aquatic system, because Cu is well known to bind with natural organic matter and served as a reducing agent during mineralization process (Karlsson et al. 2006).

Integrated approach of pollution indices

Water quality

Pollution evaluation indices such as heavy metal pollution index (HPI) and pollution index (PI) were computed individually to indicate the spatial variation of heavy metals and their contamination level in the Ajay River basin. HPI and PI were applied based on the arithmetic mean calculation of selected variables for the estimation of heavy metal contamination in water and their critical level (Fig. 5). In this study, HPI varied from 78 to

270 which indicates that majority of the sampling sites exceeded the critical value (> 100). A higher value of HPI was observed in the upper and middle parts of the river basin followed by lower basin. Similarly, PI identifies that the river water is contaminated mainly due to the high concentration of Cd, Pb, and Ni (Fig. 5). In addition, PI value for some samples showed high Cu concentration. The higher concentrations of these elements especially Cd, Cu, Pb, and Ni in the river basin is the proof of anthropogenic influences from various sources such as industrial, urban, and agricultural waste as well as mining activities, because river water received high amount of polluted sewage and effluents associated with various toxic compounds from urban industrial and centers through numerous drains. There are two important coal-bearing areas such as Raniganj and Andal present in the proximity of the Ajay River basin which spread over 443.50 km^2 of area. Mining operations have the potential to affect surface water quality and enhanced the concentrations and loads of dissolved materials because it contains a variety of contaminants such as heavy metals and metalloids. Consequently, the river might have served as an agent for the dispersion of various contaminants from its source area and
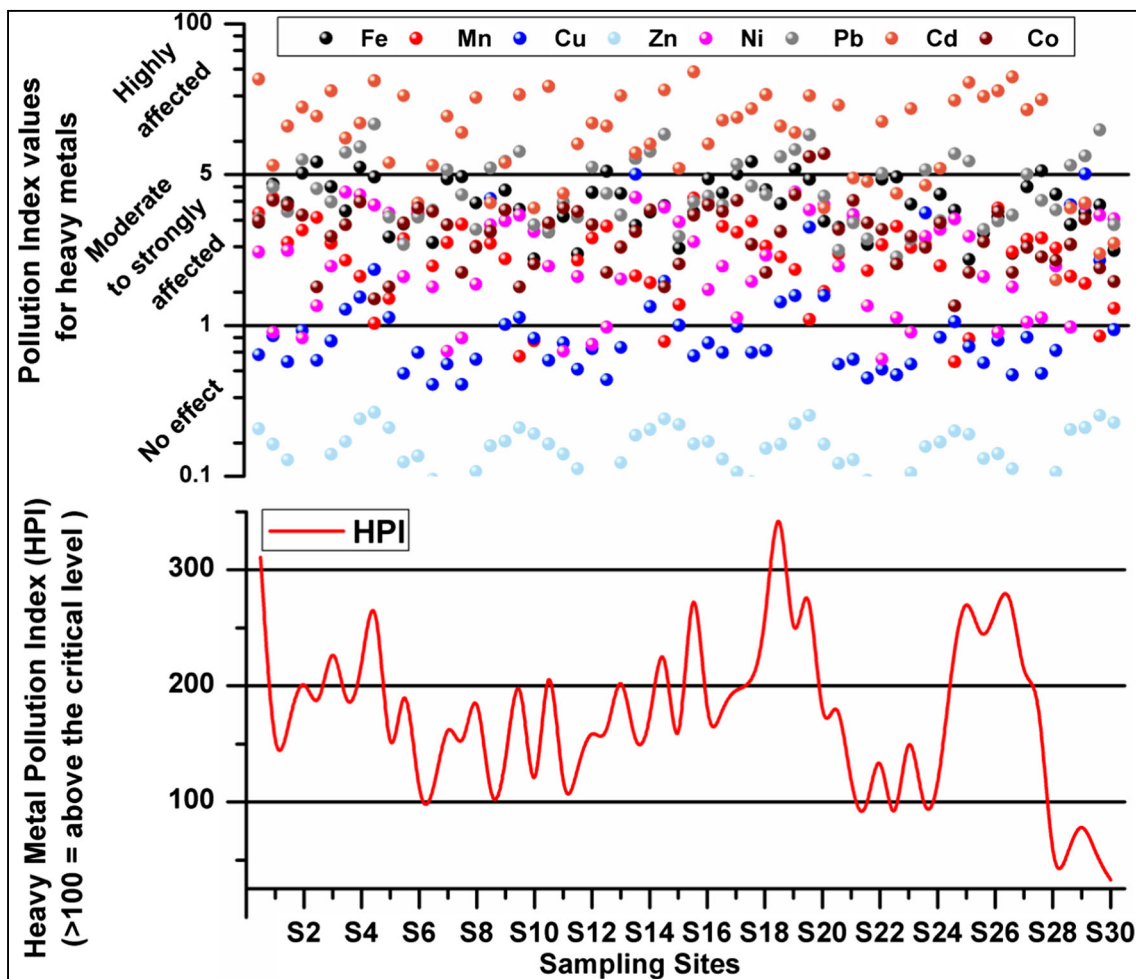

Fig. 5 Spatial distributions of pollution index (PI) and heavy metal pollution index (HPI) values along the sampling sites

responsible for the high magnitude of heavy metals throughout the river basin. These contaminants in water bodies are considered unsafe and undesirable for human health and high health risk for the regional population. We also assumed that the gradual development of industrialization and urbanization and mining activities in the proximity of river basin without proper management plan could magnify heavy metal concentrations in near future.

Sediment quality

To examine the lithogenic heavy metal contamination level in the river sediment, enrichment factor (EF) and geoaccumulation index (Igeo) have been carried out in this study (Fig. 6). EF value of particular element close to ~ 1 signifies that the element is mainly derived from geogenic sources (Chiarenzelli et al. 2001). Calculated EF values were always greater than 1.0 for the majority of elements except for Mn, suggesting a significant anthropogenic impact on heavy metals level in the river. The highest EF values were observed for Cd at all sampling sites as compared to other elements. EF value of Cu and Ni shows

moderate enrichment at all sites. Similarly, according to the Igeo values, the river basin is extremely polluted which is due to the high concentration Cd followed by Cu and Ni (Fig. 5b). The obtained values of EF and Igeo indicated that the sediment of the river basin is highly enriched with Cd, Cu, and Ni. Furthermore, moderate concentration of Pb in sediment is considered as an anthropogenic influence because Pb from the natural source appears to be very low as compared to manmade activities. High to moderate enrichment of these elements in the sediment signifies the evidence of anthropogenic contribution probably from mining activities, industrial and urban waste, and agricultural runoff. However, Fe, Co, and Zn also show moderate concentrations in the study area which mainly due to the mobilization and mineralization of iron sulfides, pyrite, and magnetite in this area (Silva et al. 2011).

Comprehensive potential risk assessment

To confirm the risks of heavy metals, we further calculated the potential ecological risk index (RI) and probable effect level (PEL)/effect range median (ERM) quotient index of sediment
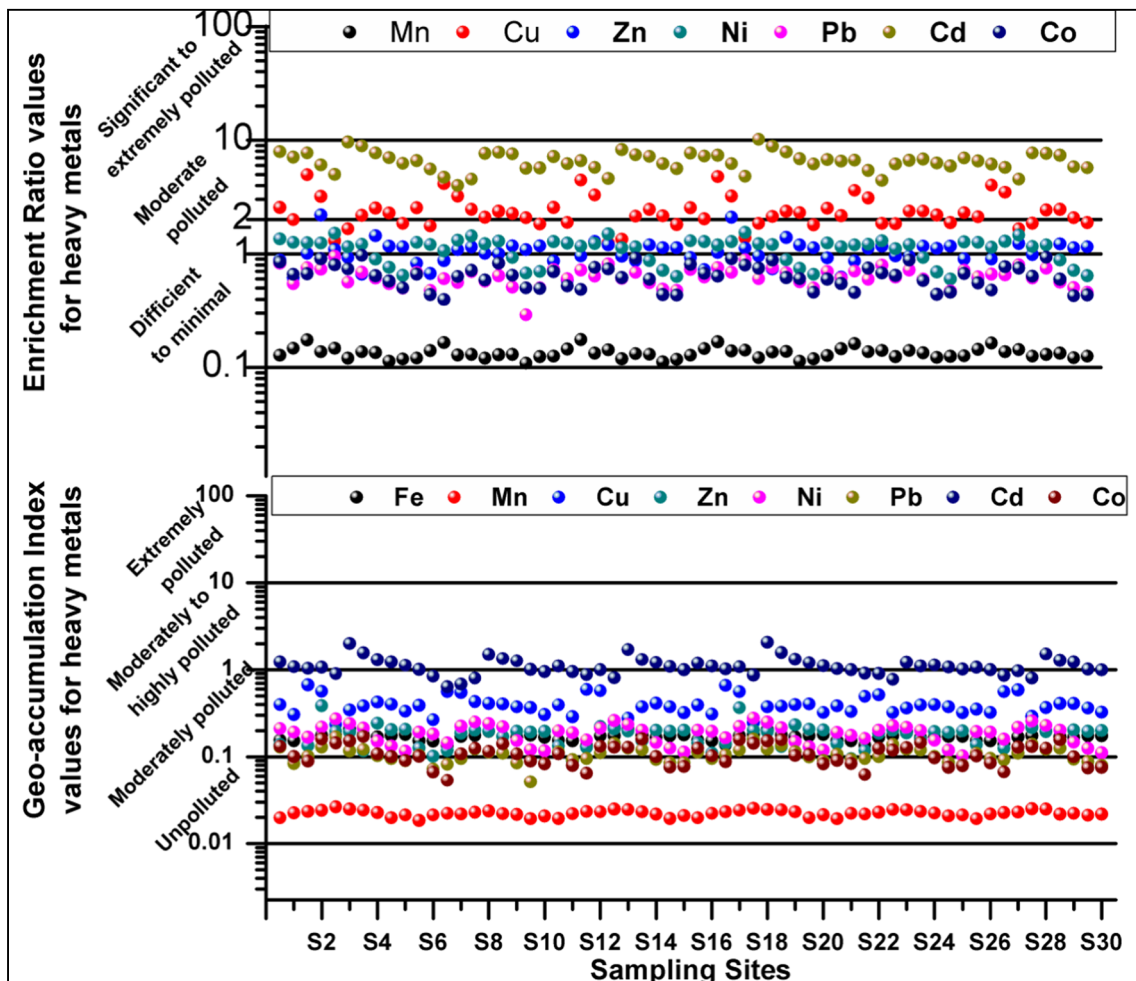

Fig. 6 Spatial distributions of enrichment ration (ER) and geoaccumulation index (Igeo) values along the sampling sites
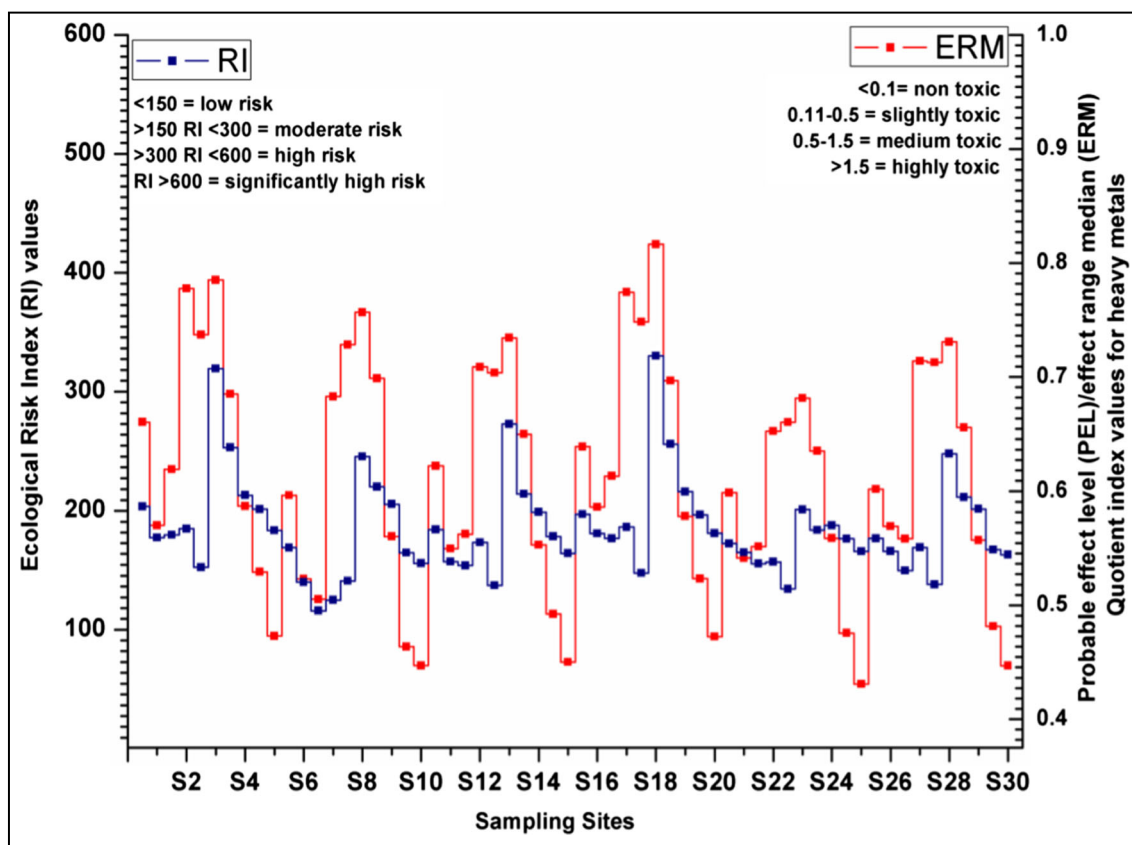
Fig. 7 Spatial distributions of ecological risk index (RI) and probable effect level (PEL)/effect range median (ERM) quotient index values along the sampling sites

samples (Fig. 7). The calculated RI value ranged from 115.85 to 329.93 indicating that the degrees of ecological risk are varied from moderate to high in this area. The high magnitudes of ecological risks have been observed in the upper part of the basin followed by the middle and lower parts of the basin. Similarly, PEL/ERM quotient index value ranges from 0.43 to 0.81 which shows that the ecological risk varies from slightly toxic to medium toxic in the study area (9b). The higher values of both indices were found in the upper, middle, and lower parts of the basin area. Several industries such as thermal power plants, locomotive industries and coal washeries, and manufacturing companies are established in urban centers like Jamtara, Chittranjan, Raniganj, and Andal. Consequently, river received a significant amount of potentially toxic elements from these areas through various outlets and plays as a carrier for dispersion of those contaminants throughout the river basin. It is interesting that majority of sampling sites have high RI and PEL/ERM quotient index values as compared to non-toxic range (< 150 and < 0.1) of both indices. However, overall results suggest that the high magnitude of Cd, Cu, and Ni in the study area poses a strong potential ecological risk for aquatic environment. In this study, the experiments like acid volatile sulfides (AVS) and simultaneously extracted metals (SEM) for the sediment samples were not conducted. Both these experiments are essential to predict the accurate metal toxicity to the ecology and local population. Based on the above considerations, this study also believed that implementation of such experiments would be helpful to trace the bioavailability of the Ajay River sediment contaminants. Therefore, these heavy metals are the key elements to be further studied which will be helpful to take appropriate measures for the polluted area of Ajay River basin.

Conclusion

This study explains the Ajay River basin characteristics based on the different physicochemical parameters and heavy metal concentrations in river water and sediment. In this study, various sources, pathways, and inter-element relationships of heavy metals have been identified. The lithological properties, weathering of mineral, agricultural waste, and urban and industrial effluents have been identified as major responsible factors that control the heavy metal concentration in the river basin. Based on the mean concentration of metals, the water and sediments of the river basin are highly contaminated especially by Cu, Cd, Pb, and Ni. It also revealed that Fe and OM significantly affect the behavior of heavy metals in the basin area. The majority of heavy metals such as Cu, Cd, Pb, and Ni are mainly derived from anthropogenic origin and are most of the widespread contaminants which pose moderate to

high potential ecological risk in the Ajay River basin. However, under this study, only the total metal concentrations have been evaluated to investigate the behavior of metals and their exposure to the ecological habitats. Based on these results, it would be very interesting in the future tests to perform a sequential experiment to estimate the exact metal bioavailability to the river aquatic organisms. Furthermore, ecological surveys of the river basin would be valuable to see how the contamination gradient has influenced ecosystem change. Additionally, this would also provide insights into the types of organisms which inhabit in this environment and what effect they might have on contaminant chemistry and exposure. Thus, to improve the current situation of Ajay River basin, adaptability measures should be introduced for ecological restoration. However, this study will be helpful to land use management, environmental risk assessment, and river basin management. In addition, integrated approach of geostatistical techniques, indices, and risk assessment should be considered for river basin management at a global standard.

References

Adamu CI, Nganje TN, Edet A (2015) Heavy metal contamination and health risk assessment associated with abandoned barite mines in Cross River State, southeastern Nigeria. Environ Nanotechnol Monit Manage 3:10–21

Akcay H, Oguz A, Karapire C (2003) Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. Water Res 37:813–822

Ali MM, Ali ML, Islam MS, Rahman MZ (2016) Preliminary assessment of heavy metals in water and sediment of Karnaphuli river. Bangladesh Environ Nanotechnol Monit Manag 5:27–35

Antunes IMHR, Neiva AMR, Albuquerque MTD, Carvalho PCS, Santos ACT, Cunha PP (2018) Potential toxic elements in stream sediments, soils and waters in an abandoned radium mine (central Portugal). Environ Geochem Health 40:521–542

APHA (2005) 2005 American Public Health Association, standard methods for the examination of water and wastewater, 21st Centennial Edn. APHA, AWWA, WPCF, Washington DC

Atibu EK, Devarajan N, Laffite A, Giuliani G, Salumu JA, Muteb RC, Mulaji CK, Otamonga JP, Elongo V, Mpiana PT, Poté J (2016) Assessment of trace metal and rare earth elements contamination in rivers around abandoned and active mine areas. The case of Lubumbashi River and Tshamilemba Canal, Katanga, Democratic Republic of the Congo. Chem Erde-Geochem 76:353–362

BIS, 2003. Bureau of Indian Standards (10500), Indian standard specification for drinking water

Bryan GW (1976) Heavy metal contamination in the sea. In: Johnston RB (ed) Marine Marine pollution. Academic Press, New York, pp 185–302

Buschmann J, Berg M, Stengel C, Winkel L, Sampson ML, Trang PTK, Viet PH (2008) Contamination of drinking water resources in the Mekong Delta floodplains: arsenic and other trace metals pose serious health risks to population. Environ Int 34(6):756–764

Caeiro S, Costa MH, Ramos TB, Fernandes F, Silveira N (2005) Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. Ecol Indic 5:151–169

Cakmak D, Perovic V, Antic-Mladenovic S, Kresovic M, Saljnikov E, Mitrovic M, Pavlovic P (2017) Contamination, risk, and source apportionment of potentially toxic microelements in river sediments and soil after extreme flooding in the Kolubara river catchment in Western Serbia. J Soils Sediments 18:1–13

Candeias C, da Silva E, Ávila P, Teixeira J (2014) Identifying sources and assessing potential risk of exposure to heavy metals and hazardous materials in mining areas: the case study of Panasqueira mine (central Portugal) as an example. Geosciences 4:240–268

Castro-Catala ND, Kuzmanovic M, Roig N, Sierra J, Ginebreda A, Barcelo D, Perez S, Petrovic M, Pico Y, Schuhmacher M, Munoz I (2016) Ecotoxicity of sediments in rivers: invertebrate community, toxicity bioassays and the toxic unit approach as complementary assessment tools. Sci Total Environ 540:297–306

Chiarenzelli JR, Aspler LB, Dunn C, Cousens B, Ozarko DL, Powis KB (2001) Multi-element and rare earth element composition of lichens, mosses, and vascular plants from the Central Barrenlands, Nunavut, Canada. Appl Geochem 16:245–270

Ciszewski D, Aleksander-Kwaterczak U, Pociecha A, Szarek-Gwiazda E, Waloszek A, Wilk-Woźniak E (2013) Small effects of a large sediment contamination with heavy metals on aquatic organisms in the vicinity of an abandoned lead and zinc mine. Environ Monit Assess 185:9825–9842

Devanesan E, Gandhi MS, Selvapandiyan M, Senthilkumar G, Ravisankar R (2017) Heavy metal and potential ecological risk assessment in sedimentscollected from Poombuhar to Karaikal coast of Tamilnadu using energy dispersive X-ray fluorescence (EDXRF) technique. Beni-Seuf Univ J Appl Sci 6:285–292

Dong Y, Ma LQ, Rhue RD (2000) Relation of enhanced Pb solubility to Fe partitioning in soils. Environ Pollut 110:515–522

Ficklin DJWH, Plumee GS, Smith KS, McHugh JB (1992) Geochemical classification of mine drainages and natural drainages in mineralized areas. In: Kharaka YK, Maest AS (eds) Water–rock interaction. Balkema, Rotterdam, pp 381–384

Gao X, Chen CTA, Wang G, Xue Q, Tang C, Chen S (2010) Environmental status of Daya Bay surface sediments inferred from a sequential extraction technique. Estuar Coast Shelf Sci 86(3):369–378

Ghosh S, Guchhait SK (2015) Characterization and evolution of primary and secondary laterites in northwestern Bengal Basin. West Bengal J Palaeogeogr 4:203–230

Ghrefat H, Yusuf N (2006) Assessing Mn, Fe, and Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. Chemosphere 65:2114–2121

Grygar TM, Elznicova J, Babek O, Hosek M, Engel Z, Kiss T (2014) Obtaining iso-chrones from pollution signals in a fluvial sediment record: a case study in a uranium-polluted floodplain of the Ploučnice river, Czech Republic. Appl Geochem 48:1–15

Gupta S, Mahato A, Roy P, Datta JK, Saha RN (2008) Geochemistry of groundwater, Burdwan District, West Bengal, India. Environ Geol 53:1271–1282

Hakanson L (1980) An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res 14:975–1001

Herojeet R, Rishi MS, Kishore N (2015) Integrated approach of heavy metal pollution indices and complexity quantification using chemometric models in the Sirsa Basin, Nalagarh valley, Himachal Pradesh, India. Chin J Geochem 34:620–633

Horton RK (1965) An index number system for rating water quality. J Water Pollut Control Fed 37:1–12

Islam MS, Ahmed MK, Raknuzzaman M, Habibullah-Al-Mamun M, Islam MK (2015) Heavy metal pollution in surface water and

sediment: a preliminary assessment of an urban river in a developing country. Ecol Indic 48:282–291

Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN (2014) Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol 7:60–72

Jha KP, Tiwari J, Singh UK, Kumar M, Subramanian V (2009) Chemical weathering and associated CO 2 consumption in the Godavari river basin, India. Chem Geol J 264:364–374

Jiang M, Zeng G, Zhang C, Ma X, Chen M, Zhang J, Lu L, Yu Q, Hu L, Liu L (2013) Assessment of heavy metal contamination in the surrounding soils and surface sediments in Xiawangang River, Qingshuitang District. PLoS One 8:e71176

Joshi DM, Kumar A, Agrawal N (2009) Studies on physicochemical parameters to assess the water quality of river ganga for drinking purpose in Haridwar district. Rasayan J Chem 2:195–203

Karlsson T, Persson P, Skyllberg U (2006) Complexation of copper (ii) in organic soils and in dissolved organic matter-EXAFS evidence for chelate ring structures. Environ Sci Technol 40:2623–2628

Kumar B, Singh UK, Ojha SN 2018 Evaluation of geochemical data of Yamuna River using WQI and multivariate statistical analyses: a case study. Int J River Basin Manag, 1–13

Kumar B, Singh UK, Mukherjee I (2017) Hydrogeological influence on the transport and fate of contaminants in the groundwater, India. JSM Biol 2:1–11

Kumar B, Singh UK, Mukherjee I, Daas MS (2016) Water quality status of Indian major rivers with reference to agriculture and drinking purposes. Raman VAV (ed.) Geoanthropogenic environment: an appraisal. A.K. Publications, pp. 65–81

Kumar B, Singh UK, Padhy PK, 2014 Water quality assessment of Ajay River with reference to suitability for agriculture purposes. Environica-1 Levent Book publisher, pp. 121–127

Kumar R, Rani M, Gupta H, Gupta B (2015) Trace metal fractionation in water and sediments of an urban river stretch. Trace metal fractionation in water and sediments of an urban river stretch. Chem Speciat Bioavailab 26:200–209

Liu X, Song Q, Tang Y, Li W, Xu J, Wu J, Wang F, Charles P (2013) Human health risk assessment of heavy metals in soil—vegetable system: a multi-medium analysis. Sci Total Environ 463:530–540

Lohani MB, Singh A, Rupainwar DC, Dhar DN (2008) Seasonal variations of heavy metal contamination in river Gomti of Lucknow city region. Environ Monit Assess 147:253–263

Long ER, Macdonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manag 19:81–97

Ma X, Zuo H, Tian M, Zhang L, Meng J, Zhou X (2016) Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. Chemosphere 144:264–272

Maanan M, Saddik M, Maanan M, Chaibi M, Assobhei O, Zourarah B (2014) Environmental and ecological risk assessment of heavy metals in sediments of Nador lagoon. Morocco Ecol Indic 48:616–626. https://doi.org/10.1016/j.ecolind.2014.09.034

Martinez-Santos M, Probst A, Garcia-Garcia J, Ruiz-Romera E (2015) Influence of anthropogenic inputs and a high-magnitude flood event on metal contamination pattern in surface bottom sediments from the Deba River urban catchment. Sci Total Environ 514:10–25

Mellis EV, Cristina M, Casagrande JC, Níquel ADE, Solos EM, Funçao EM, Orgânica M, Ferro EÓDE (2004) Nickel adsorption by soils in relation to pH, organic matter, and iron oxides. Sci Agric 61:190–195

Milacic R, Zuliani T, Vidmar J, Oprckal P, Ssancar J (2017) Potentially toxic elements in water and sediments of the Sava River under extreme flow events. Sci Total Environ 605:894–905

Mohamaden MI, Khalil MK, Draz SE, Hamoda AZ (2017) Ecological risk assessment and spatial distribution of some heavy metals in surface sediments of New Valley, Western Desert, Egypt. Egypt J Aquat Res 43:31–43

Muller G (1979) Heavy metals in the sediment of the Rhine-Changes Seity. Umschau in Wissenschaft und Technik 79:778–783

Nethaji S, Kalaivanan R, Viswam A, Jayaprakash M (2016) Geochemical assessment of heavy metals pollution in surface sediments of Vellar and Coleroon estuaries, Southeast coast of India. Mar Pollut Bull 115:469–479

Neyestani MR, Bastami KD, Esmaeilzadeh M, Shemirani F, Khazaali A, Molamohyeddin N, Afkhami M, Nourbakhsh S, Dehghani M, Aghaei S, Firouzbakht M (2016) Geochemical speciation and ecological risk assessment of selected metals in the surface sediments of the northern Persian Gulf. Mar Pollut Bull 109(1):603–611

NIH (1999) National Institute of Hydrology (NIH) technical report, SR-2/98-99, hydrological inventory of South Bihar River Basin. Author, "Chatterjee, C., Ghosh, N.C.S." NIH, Jal Vigyan Bhavan, RoorKee, India

Pandey B, Suthar S, Singh V (2016) Accumulation and health risk of heavy metals in sugarcane irrigated with industrial effluent in some rural areas of Uttarakhand, India. Process Saf Environ Prot 102:655–666

Pandey M, Pandey AK, Mishra A, Tripathi BD (2015) Assessment of metal species in river Ganga sediment at Varanasi, India, using sequential extraction procedure and SEM-EDS. Chemosphere 134:466–474

Prasad B, Bose JM (2001) Evaluation of heavy metal pollution index for surface and spring water near a limestone mining area of the lower Himalayas. Environ Geol 41:183–188

Prashanth L, Kattapagari KK, Chitturi RT, Baddam VRR, Prasad LK (2015) A review on role of essential trace elements in health and disease. J Dr NTR Univ Health Sci 4:75

Qasim B, Motelica-Heino M (2014) Potentially toxic element fractionation in technosoils using two sequential extraction schemes. Environ Sci Pollut Res 21:5054–5065

Rajmohan N, Prathapar SA, Jayaprakash M, Nagarajan R (2014) Vertical distribution of heavy metals in soil profile in a seasonally water logging agriculture field in Eastern Ganges Basin. Environ Monit Assess 186:5411–5427

Reader HE, Stedmon CA, Kritzberg ES (2014) Seasonal contribution of terrestrial organic matter and biological oxygen demand to the Baltic Sea from three contrasting river catchments. Biogeosciences 11:3409–3419

Rieuwerts JS, Thornton I, Farago ME, Ashmore MR (2015) Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. Chem Speciat Bioavailab 10:61–75

Roy S (2012) Spatial variation of floods in the lower Ajay River basin, West Bengal: a geo-hydrological analysis. Int J Remote Sens GIS 1:132–144

Saha, D.K., Naskar, D.C., 2002. Report on geoenvironmental appraisal in parts of Damodar, Ajay interfluve including Asansol and Durgapur areas for development activities of Adda and WBPCB Government of India Geologzal Survey of India, Central Geophysics Division Gsi-chq-35164

Sakan S, Devic G, Relic D, Andelkovic I, Sakan N, Đordevic D (2015) Aquatic sediments pollution estimate using the metal fractionation, secondary phase enrichment factor calculation, and used statistical methods. Environ Geochem Health 37:97–113

Salomons W, Forstner U, 1984. Metals in the hydrocycle. EOS Trans Am Geophys Union 66

Sharma HS, Chattopadhyay S (1998) Sustainable development issues and case studies. Concept Publishing Company, New Delhi

Sharma S, Jha PK, Ranjan MR (2017) Water quality monitoring of Yamuna River by using GIS based water quality index in Delhi, India. Int J Curr Microbiol App Sci 6:1249–1263

Shetye SS, Sudhakar M, Mohan R, Tyagi A (2009) Implications of organic carbon, trace elemental and CaCO₃ variations in a sediment core from the Arabian Sea. Indian J Mar Sci 38:432–438

Shreshtha S, Kazama F (2007) Assessment of surface water quality using multi-variate statistical technique: a case study of Fuji River basin. J Environ Mode Soft 22:464–475

Shumilin E, Gordeev V, Choumiline K (2011) Assessment of geochemical mobility of metals in surface sediments of the Santa Rosalia mining region, Western Gulf of California. Arch Environ Contam Toxicol 60:8–25

Silva LFO, Querol X, da Boit KM, Vallejuelo SFO, de Madariaga JM (2011) Brazilian coal mining residues and sulphide oxidation by Fenton's reaction: an accelerated weathering procedure to evaluate possible environmental impact. J Hazard Mater 186:516–525

Singh J, Kalamdhad AS (2018) Effects of heavy metals on the environment by utilization of urban waste compost for land application: a review. In urban ecology, water quality and climate change. Springer, Cham, pp 329–340

Singh UK, Kumar B (2017) Pathways of heavy metals contamination and associated human health risk in Ajay River basin, India. Chemosphere 174:183–199

Singh UK, Ramanathan AL, Subramanian V (2018) Groundwater chemistry and human health risk assessment in the mining region of East Singhbhum, Jharkhand, India. Chemosphere 204:501–513

Sipos P, Choi C, Németh T, Szalai Z, Poka T (2014) Relationship between iron and trace metal fractionation in soils. Chem Speciat Bioavailab 2299:20–30

Siudek P, Frankowski M, Siepak J (2015) Trace element distribution in the snow cover from an urban area in Central Poland. Environ Monit Assess 187:1–15

Smith SL, MacDonald DD, Keenleyside KA, Ingersoll CG, Field J (1996) A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. J Great Lakes Res 22:624–638

Soliman NF, Nasr SM, Okbah MA (2015) Potential ecological risk of heavy metals in sediments from the Mediterranean coast, Egypt. J Environ Health Sci Eng 13:70 1–12

Strady E, Dinh QT, Nemery J, Nguyen TN, Guédron S, Nguyen NS, Denis H, Nguyen PD (2017) Spatial variation and risk assessment of trace metals in water and sediment of the Mekong Delta. Chemosphere 179:367–378

Tian K, Huang B, Xing Z, Hu W (2017) Geochemical baseline establishment and ecological risk evaluation of heavy metals in greenhouse soils from Dongtai, China. Ecol Indic 72:510–520

Torri SI, Correa RS (2012) Downward movement of potentially toxic elements in biosolids amended soils. Appl Environ Soil Sci 2012: 1–7

Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. Geol Soc Am Bull 72:175–192

Ungureanu T, Iancu GO, Pintilei M, Marius M (2016) Spatial distribution and geochemistry of heavy metals in soils: a case study from the NE area of Vaslui County. Rom J Geochem Explor 176:20–32

USEPA (1992) Sediment classification methods compendium. United States Environmental Protection Agency (USEPA), EPA 823-R-92-006, Office of Water, Washington, DC, p 222

Vu CT, Lin C, Shern C, Yeh G, Le VG, Tran HT (2017) Contamination, ecological risk and source apportionment of heavy metals in sediments and water of a contaminated river in Taiwan. Ecol Indic 82: 32–42

Wang B, Wang Y, Wang W (2014) Retention and mitigation of metals in sediment, soil, water, and plant of a newly constructed root-channel wetland (China) from slightly polluted source water. Springerplus 3: 326

Wang J, Liu G, Lu L, Zhang J, Liu H (2015) Geochemical normalization and assessment of heavy metals (Cu, Pb, Zn, and Ni) in sediments from the Huaihe River, Anhui, China. Catena 129:30–38

Wang W, Wang W (2017) Trace metal behavior in sediments of Jiulong River Estuary and implication for benthic exchange fluxes. Environ Pollut 225:1–12

WHO (2006) World health organization (WHO), guidelines for drinking water quality, 3rd edition. World Health Organization, Geneva, pp 488–449

Wu B, Zhao DY, Jia HY, Zhang Y, Zhang XX, Cheng SP (2009) Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing section, China. Bull Environ Contam Toxicol 82:405–409. https://doi.org/10.1007/s00128-008-9497-3

Xu ZQ, Ni SJ, Tuo XG (2008) Calculation of heavy metals toxicity coefficient in the evaluation of potential ecological risk index. Environ Sci Technol 31:112–115

Yi Y, Yang Z, Zhang S (2011) Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. Environ Pollut 159(10):2575–2585

Zhang Z, Juying L, Mamat Z, Qingfu Y (2016) Sources identification and pollution evaluation of heavy metals in the surface sediments of Bortala River, Northwest China. Ecotoxicol Environ Saf 126:94–101