

Sequential extraction and risk assessment of pollutants from one major tributary of the Ganga

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ABSTRACT

The geochemical fractionation of toxic heavy metals Cd, Pb, Cr, Co, Mn, Ni, Cu, Fe and Zn was investigated in 10 different sites of river bed sediments (up, mid and downstream) of Gomti River at Lucknow city. Sequential extraction technique was used to identify the distribution of trace elements binding in different fractions; i.e., exchangeable, carbonate, Fe and Mn oxide, organic matter and residual. Heavy metal concentrations were least at upstream and significantly higher in mid and downstream. Fractionation indicated that dominant metals were bound in residual fraction to the bed sediments except for Cd and Pb, which were bound in an equivalent fraction. Geo-accumulation index factor reveals that the enrichment of heavy metals in the bio-available fraction is contributed anthropogenically. Hierarchical cluster analysis also shows the metal pollution load in the river. Risk assessment code of Cd and Ni showed very high risk (ranged from 54.41 to 85.56 and 20.57 to 44.92 respectively) followed by Pb (high risk), Zn, Co (medium risk), Cr, Mn, Cu, Fe (low risk) in Gomti River water. Further, concentrations of Cd and Pb at mid Lucknow were 31 and 75%, high enough to pose a substantial risk to the environment.

Key words: cluster analysis, heavy metal, risk assessment, river water quality, sequential extraction

HIGHLIGHTS

- The geochemical fractionations of toxic heavy metals were investigated.
- Sequential extraction technique was used to identify the distribution of trace metals binding in different fractions.
- Geo-accumulation index factor reveals that the enrichment of heavy metals in the bio-available fraction is contributed anthropogenically.
- Hierarchical cluster analysis also shows the metal pollution load in the river.

1. INTRODUCTION

Water is an essential life supporting component. When it gets contaminated or infected, it adversely affects human beings and other organisms (Markandeya *et al.* 2021; Pandey *et al.* 2021). Heavy metals are one of the major contaminants that pose serious problems not only in a river body but in any medium due their persistent nature and non-biodegradable properties (Kisku *et al.* 2016; Ostad-Ali-Askar *et al.* 2018). The contaminants such as metal and others are introduced into the river eco-system as a result of volcanic eruptions, weathering of rocks, and from a variety of human activities such as disposal of domestic sewage, mining, dredging, processing and use of vehicles, metals and substances containing metals (Bashir *et al.* 2020). The maximum average of risk was due to lead and copper with the respective values of 60.10×10^{-7} and 33.99×10^{-7} from some targeted wells (Saleh *et al.* 2019). River sediments are not only the sink of heavy metals but also reflect the history of river pollution by deposition of various metals in river sediments (Cui *et al.* 2019; Jafarzadeh *et al.* 2022). Sometimes, partitioning of heavy metals is used to provide information on binding sites, their source and pathways by which metals are transported to the aquatic environment (Masindi & Muedi 2018; Mohammadi *et al.* 2020; Nawrot *et al.* 2020).

In sediments, heavy metals are present in various chemical forms and exhibit different chemical and physical behaviors in terms of chemical interaction, biological availability, mobility and potential toxicity (Palansooriya *et al.* 2020; Pant *et al.* 2021). The non-residual, including exchangeable, oxidizable and reducible heavy metals are considered to be the mobile or environmentally reactive fraction with respect to geological and chemical processes (Kumar *et al.* 2017a, 2017b;

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Wijaya *et al.* 2019). It is unlikely for residual metals to be released into a solution phase through dissolution and remain fixed in sediments within the matrix of silicates and other detrital minerals (Amor *et al.* 2019). It is also supposed that more soluble metals are more bioavailable and vice versa. Further, sediment is an important segment and chief source of heavy metals in floating or riverine ecosystems (Tiwari & Kisku 2016; Huang *et al.* 2019).

When a contaminated area is dredged and placed on land, contaminated sediments pose the following two types of risk to the environment: first, ecological risk to aquatic life and second, toxic risks to terrestrial habitat (Kulbat & Sokolowski 2019). More unstable conditions of the aquatic ecosystem occur, when there is seasonal flooding or storms, or bioturbation due to movement and feeding of benthic organisms. Also, activities such as dredging result in major sediment disturbances, leading to changes in the chemical properties of the sediment (Massolo *et al.* 2012). Environmental and health effects of heavy metals in sediments depend on mobility and bioavailability of metals, which are the function of their partitioning with sediments (Devi & Bhattacharyya 2018). Further, these contaminants are considered to be one of the greatest threats to human health and aquatic life, due to their toxic effects on the environment (Tchounwou *et al.* 2012; Markandeya *et al.* 2017). Quantification of total metal concentration alone, however, is not enough evidence of a potential toxic effect of heavy metals and the relationship between metal concentration and their bioavailability is not clearly established (Egorova & Ananikov 2017). It is the need of the hour to identify and quantify the mode of occurrence of contaminants in which a metal is present in the sediment, in order to gain a more accurate understanding of the actual and potential impacts of the prominent level of metals in sediments and to appraise the processes of downstream transport, deposition and release under changing conditions of the environment (Ali *et al.* 2019). Organic matter plays a major role in the accumulation of metals in sediment, their availability to the receptors, toxicity to the plants and sediment organisms and transmission to the groundwater. The knowledge of the path of metal binding and their long-term behavior under the conditions of impact of different natural and anthropogenic factors are important for understanding the processes affecting metal mobility and bioavailability in soils with organic matter (Palansooriya *et al.* 2020).

In the present study, an attempt has been made to quantify the level of trace metals in the water and bed sediments both in the mobile and bound phases of Gomti River. Further, the eco-toxicological potential of the metals (Cr, Cu, Fe, Cd, Pb, Ni, Mn, Co and Zn) have also been determined. Moreover, fractionable percentage of bioavailability of heavy metals has assessed the dynamics and mobility factor in different geochemical fractions as well as risk assessment. To assess anthropogenic contamination in water bodies, the geo-accumulation index has also been calculated.

2. MATERIALS AND METHODS

2.1. Sampling sites

Gomti River originates from Gomat Taal situated in Pilibheet district of Uttar Pradesh, India. The river travels nearly 730 km passing through the different cities of Uttar Pradesh and merges into river Ganga at Kaithi in Ghazipur district. Lucknow city is situated (26.8467° N and 80.9462° E) on the bank of river Gomti and it serves as one of the major sources of drinking water (about 800 million liters per day) for Lucknowites and people of the surrounding areas. According to the census 2011, the population of about more than 3.5 million is served by the river in different ways. A total of 10 locations [viz. upstream-Ghaila bridge (site-1), Gau ghat (site-2), Kudiya ghat (site-3), mid-Lucknow-Daliganj bridge (site-4), Hanuman setu (site-5), Nisatganj bridge (site-6), Khatu Shyam asharam (site-7), Gomti bairaj (site-8), Dilkusha garden (site-9) and downstream-Saheed path (site-10)] were selected on the basis of the load of pollutant sources in the stream (Figure 1).

2.2. Sample collection and pretreatment

The grab samples of water and bed sediments (20 cm below the surface) were collected in polyethylene bags from each of the selected locations during March to May 2019. The sediment samples were collected from three points (left, right and middle) across the river width at each of the 10 locations and background samples (control) were collected from 10 km before entry point at Lucknow city. The collected sediment samples were air dried, large unwanted particles were hand picked and the rest were ground with mortar and pestle for the original sample in powdery form. To prevent further microbial degradation, pH of the river water samples was adjusted up to 2. For further analyses, water and sediment samples were transported to the laboratory in ice box under low temperature (4 °C) conditions and analyzed according to APHA/AWWA WEF (2012).

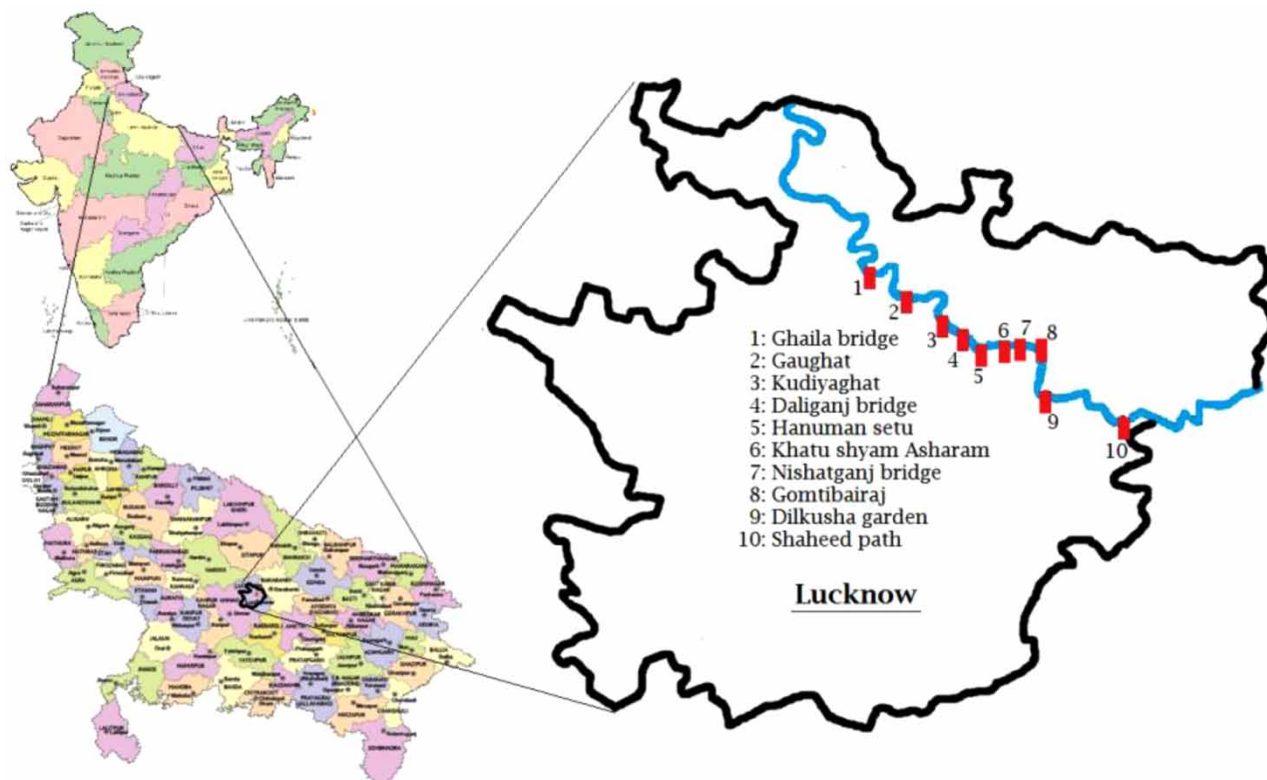


Figure 1 | Map of the study area and showing the locations at Lucknow.

2.3. Quality control and assurance

AR grade chemicals and reagents were used without any further purification or disturbance (Merck and Sigma-Aldrich, Germany: 99.9% purity). Glass wares used were washed with 1.15 N nitric acid followed by distilled water for several times. The quality assurance measures included meticulous infectivity control (stringent washing/ cleaning procedures), monitoring of blank levels of solvents, equipment and other materials. All the analyses were carried out in triplicate form and the recoveries of mix metal standards were determined 75–95% through the spiked sample method and standard solutions were stored at 4 °C before further use.

2.4. Samples preparation and analysis

pH of Gomti river water and sediment samples were analyzed by using APHA/AWWA (2012). The total organic matter of the sediment was determined using the back titration method (Walkley & Black 1934). The sample for the metal speciation study was dried at 100 °C and passed through 230 mesh number as per ASTM. The air dried samples were sieved to obtain 75 mm sediment fraction. The analysis of metal concentration was done using Atomic Absorption Spectroscopy (AAS, Model GBC Avanta-Sigma, Australia). Hollow cathode lamps (Varian) for respective metals were used at a working current ranging from 5–30 mA with 213.9–357.9 nm spectral line. The procedure of Tessier *et al.* (1979) was used for the speciation study except that water soluble and plant available fractions were included in this process. Thus, the sediment samples were subjected to a five stage process to extract and separate Cd, Pb, Cr, Co, Mn, Ni, Cu, Fe and Zn through exchangeable, bound to carbonate, bound to Mn/Fe oxides, bound to organic matter and residual fractions.

2.5. Risk assessment

The possible environmental and ecological risks of the heavy metals in the sediments were assessed by calculating risk factors; that is, geo-accumulation index (I_{geo}), mobility factor (MF) of metals and risk assessment code (RAC) to find out the status of pollutants risk in bed sediment.

2.6. Geo-accumulation index (I_{geo})

Geo-accumulation index (I_{geo}), which is widely used for evaluating the quantity of metal contamination or pollution in soil/sediment samples of terrestrial or aquatic environments, was applied to assess the pollution status of the studied area. It is a quantitative measure of metal pollution (Muller 1979). This assessment index has been calculated in soils and sediments by Equation (1) (Abraham & Parker 2008; Shi *et al.* 2010):

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5 B_n} \quad (1)$$

where B_n is the background value of the clear water sample, 1.5 is the background matrix correction factor and C_n is the total heavy metal concentration in the sediment sample.

2.7. Mobility factor of metals in bed-sediment

Mobility factor provides an indication of the bio-availability or non-bioavailability of the metal. This process may be assessed as the ratio of the concentration of metals in re-mobilizable fractions to the combined concentration in all geochemical fractions. In this, a 5-stage sequential extraction procedure was used. F-1 is the exchangeable fraction, F-2 is the carbonate fraction, F-3 is the Fe-Mn oxide fraction, F-4 is the organic fraction and F-5 is the residual fraction. Based on their proposal, the mobility factor of metals may be obtained using Equation (2). The mobility of metals in sediments may be evaluated by the absolute and relative content of fractions weakly bound to the sediment components (Jokinen *et al.* 2020). The mobility factor (MF) was calculated using relative index as per the following Equation (2):

$$MF = \frac{F-1 + F-2}{F-1 + F-2 + F-3 + F-4 + F-5} \quad (2)$$

where F-1 is the exchangeable fraction; F-2 is the carbonate fraction; F-3 is the Fe-Mn oxide fraction; F-4 is the organic fraction and F-5 is the residual fraction.

2.8. Risk assessment code (RAC)

Risk assessment code (RAC), which was originally developed by Perin *et al.* (1985), is widely used in ecological risk assessment of heavy metals in sediments. RAC classification is based on the bonding between metals and different geochemical fractions present in sediments, which may be released and enter into the food chain. In the present study, RAC is being used to assess the risk of heavy metals in surface sediments of the Gomti River. It further assesses the possible release of heavy metals in solution based on the percentage of exchangeable and carbonate fractions in sediments and the model value to calculate RAC is given in the following Equation (3) (Tang *et al.* 2010).

$$RAC = \text{Exchangeable Fraction \%} + \text{Carbonate Fraction \%} \quad (3)$$

2.9. Statistical analysis

The level of significance was calculated by one-way ANOVA in the analysis of variance. Sigma state 3.5 was applied for calculation of least standard deviation (LSD) and pair-wise comparison was assessed by Paliwal comparison method.

2.10. Factor analysis/principal component analysis

This is a multivariate statistical technique, which attempts to find out the gravity of a particular factor lower dimensional linear structure from the data set. These factors can be interpreted in terms of new variables. It is also used to simplify the dataset (Cattel 1965). The first principal component is oriented such that it explains about 75% of the variance. Then the second principal component is oriented to explain the remaining 10% variance. In factor analysis, one chooses the number of components up front and then seeks to orient them together so that in sum they explain as much of the total variance as possible.

2.11. Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is a multivariate statistical technique, which classifies the parameters into clusters based on their similarities represented in the dendrogram. HCA classifies water quality parameters into different groups so that variables

within a cluster start with the most similar pair of variables and form higher clusters step by step. To yield different clusters of the data set, the dendrogram can be fragmented at different levels. Each fragmented level provides a visual summary of the cluster through a picture of the groups and their proximity with a dramatic reduction in dimensionality of the original data (Leal *et al.* 2016). In this study, the Ward's method is used to evaluate distance between clusters (Bhardwaj & Parmar 2020).

3. RESULTS AND DISCUSSION

3.1. Organic matter (OM) and pH in bed-sediment

The results indicate that organic matter in bed sediment ranges from 0.95 to 7.98%. The organic matter content in background sediment was 0.795%, while the ordinary organic carbon of the city area was 1.9%, which was nearly two and a half times greater than the normal that showed an organic load of the river in the city area. In the background (control), pH of the water sample was 7.53, whereas river water pH was found to range from 7.56 to 8.20 while bed sediment pH ranged from 7.98 to 8.51. The average pH of river water was 7.89 in city area while background pH of river water and bed sediments was found within the acceptable limit. pH is an important factor for determination of water quality and the extent of pollution in the river system. A pH range of 6.5–8.5 is typically acceptable as per the guidelines suggested by WHO (2011). Kumar *et al.* (2020) also found that pH of the river water was found to be higher than the normal value.

3.2. Heavy metals concentration in river water and its bed-sediment

The average concentration of heavy metals; that is, Cd, Pb, Cr, Co, Mn, Ni, Cu, Fe and Zn of the background sample in river water were below detection limit (BDL), 0.30, 0.029, BDL, 0.18, 0.25, 0.38, 1.01 and 0.11 mg/L respectively. In river water Cd, Pb, Cr, Co, Mn, Ni, Cu, Fe and Zn concentrations ranged from BDL to 0.31, 0.32 to 1.02, 0.03 to 0.33, BDL to 0.33, 0.68 to 2.86, 0.27 to 0.56, 0.53 to 1.63, 1.16 to 6.98 and 0.49 to 1.03 mg/L, respectively, while in bed-sediment these values ranged from 2.21 to 16.96, 5.63 to 38.34, 4.55 to 26.53, 1.08 to 8.94, 76.57 to 114.7, 2.12 to 23.02, 21.14 to 87.48, 877 to 2,255 and 56.30 to 165.28 µg/g, respectively (Tables 1 and 2). The minimum concentration of heavy metals was observed in upstream (site 1 and 2), while the maximum concentration was observed in midstream (site 7 and 8). In the present study, heavy metal (i.e., Cd, Pb, Cr, Co, Mn, Ni, Cu, Fe and Zn) concentration in river water and bed sediments in the city area were found to be manyfold higher than the background sample. This may be due to direct drainage of both sewage and industrial effluents to the river without proper treatment. Kumar *et al.* (2020) also found the load of heavy metals in river water and sediment samples in concentrated amount, which is supporting the present study.

The river receives a high volume of mixed domestic as well as industrial wastewater into the midstream. Moreover, a barrage is constructed in the midstream of site-8, which inhibits the flow of river water causing the deposition of suspended matter in that area. This contaminated stretch poses the highest risk to the aquatic environment as a source of pollution. Kisku *et al.* (2016) have also reported similar findings. High concentrations of heavy metals have been found in the sediments. Ali *et al.* (2019) have also found the load of heavy metals in river sediment samples, which supports the present study. The major accumulation mechanism of heavy metals in sediments leads to the existence of five categories; exchangeable, bound to reducible phases (Fe and Mn oxide), carbonate, organic matter and residual. These categories have different remobilization behaviors under varying environmental conditions. The adsorptive and exchangeable fractions are a consequence of human activity. The carbonate bound fractions are considered to have a weak link and may equilibrate with aqueous phase, thus becoming more readily bioavailable. The combination of Fe/Mn oxide and the organic matter have a scavenging effect and may provide a sink for heavy metals (Guan *et al.* 2018).

3.3. Sequential fraction percentage of heavy metals in bed-sediments

Sequential fraction showed that maximum fraction of Cd (60.32%) in sediments was in the exchangeable bound form, which significantly decreased in the carbonate phase (12.7%), Fe/Mn oxide phase (9.63%), organic matter phase (10.88%) and residual phase (6.47%), respectively. Thus, the sequential fraction of Cd in the bed sediments followed the sequence exchangeable > carbonate > organic > Fe/Mn oxide > residual. Bioavailable forms of Cd in bed sediment ranged from 54.41% to 85.56% while non-available ranged from 14.44% to 45.59% (Table 3).

Maximum amount of Pb was available in exchangeable bound form (45.96%), which significantly decreased in different fractions like the Fe/Mn oxide (23.42%), residual (19.53%), carbonate phase (7.68%) and organic matter phase (3.41%), respectively. Thus, Pb in the bed sediments was bound to a different phase in the sequence as exchangeable > Fe/Mn oxide

Table 1 | Heavy metal concentrations (mg/L) in water

Sites	Cd	Pb	Cr	Co	Mn	Ni	Cu	Fe	Zn
S-1	BDL	0.45 ± 0.12	0.031 ± 0.006	BDL	0.68 ± 0.0606	0.27 ± 0.031	0.53 ± 0.051	1.06 ± 0.491	0.56 ± 0.049
S-2	0.04 ± 0.0013	0.66 ± 0.019	0.331 ± 0.012	0.28 ± 0.044	2.84 ± 0.375	0.56 ± 0.026	1.63 ± 0.323	6.38 ± 0.866	1.03 ± 0.219
S-3	0.31 ± 0.008	0.37 ± 0.009	0.078 ± 0.011	0.26 ± 0.006	1.06 ± 0.155	0.41 ± 0.039	1.05 ± 0.086	5.24 ± 0.774	0.64 ± 0.043
S-4	0.26 ± 0.0065	0.58 ± 0.020	0.074 ± 0.006	BDL	1.25 ± 0.173	0.43 ± 0.034	0.96 ± 0.049	3.95 ± 0.433	0.58 ± 0.037
S-5	BDL	0.32 ± 0.012	0.046 ± 0.012	BDL	0.87 ± 0.081	0.28 ± 0.022	0.86 ± 0.037	3.05 ± 0.393	0.49 ± 0.054
S-6	0.025 ± 0.0069	0.44 ± 0.014	0.068 ± 0.005	BDL	1.01 ± 0.057	0.36 ± 0.031	0.74 ± 0.144	2.98 ± 0.144	0.55 ± 0.039
S-7	0.29 ± 0.0185	0.58 ± 0.024	0.062 ± 0.006	BDL	0.98 ± 0.037	0.41 ± 0.037	0.92 ± 0.162	4.58 ± 0.751	0.63 ± 0.032
S-8	0.28 ± 0.0092	0.49 ± 0.020	0.071 ± 0.0115	BDL	1.12 ± 0.202	0.43 ± 0.052	0.77 ± 0.104	6.98 ± 1.039	0.75 ± 0.026
S-9	0.31 ± 0.032	1.02 ± 0.043	0.152 ± 0.026	0.33 ± 0.007	1.57 ± 0.162	0.45 ± 0.019	1.01 ± 0.202	6.22 ± 0.779	0.88 ± 0.104
S-10	0.13 ± 0.0052	0.52 ± 0.020	0.101 ± 0.0104	0.31 ± 0.014	1.32 ± 0.086	0.38 ± 0.037	0.89 ± 0.031	4.55 ± 0.722	0.71 ± 0.049
Mean	0.21	0.54	0.10	0.30	1.27	0.40	0.94	4.51	0.68
LSD ($\alpha = 0.05$)	0.0375	0.0641	0.0361	0.048	0.496	0.101	0.436	2.037	0.253
BG	BDL	0.30 ± 0.017	0.029 ± 0.005	BDL	0.18 ± 0.03	0.25 ± 0.031	0.38 ± 0.04	1.01 ± 0.08	0.11 ± 0.01

Note: BDL, below detection limit (BDL); ± indicate the standard error mean (SEM), least standard deviation (LSD) and Background Sample (BS).

Table 2 | Heavy metals concentration ($\mu\text{g/g}$) in sediment

Sites	Cd	Pb	Cr	Co	Mn	Ni	Cu	Fe	Zn
S-1	2.21 \pm 0.312	5.63 \pm 0.491	4.552 \pm 0.43	1.08 \pm 0.144	84.45 \pm 2.021	2.819 \pm 0.306	25.36 \pm 1.039	877 \pm 6.93	56.3 \pm 1.44
S-2	8.35 \pm 0.606	15.85 \pm 1.38	12.25 \pm 0.889	6.34 \pm 0.491	76.57 \pm 1.617	2.121 \pm 0.358	71.28 \pm 2.021	1,874 \pm 8.66	123.5 \pm 3.92
S-3	5.08 \pm 0.30	10.52 \pm 0.664	10.86 \pm 0.76	3.84 \pm 0.37	110.9 \pm 3.23	9.228 \pm 0.606	41.39 \pm 1.415	1,537 \pm 10.39	105.4 \pm 2.77
S-4	11.2 \pm 1.44	12.05 \pm 1.06	9.057 \pm 0.491	2.48 \pm 0.49	85.22 \pm 2.59	8.386 \pm 0.514	48.61 \pm 2.229	1,374 \pm 8.08	98.24 \pm 2.02
S-5	16.96 \pm 1.03	17.82 \pm 1.45	14.14 \pm 1.44	4.18 \pm 0.185	94.44 \pm 2.19	10.7 \pm 0.889	39.25 \pm 0.866	1,040 \pm 9.23	56.87 \pm 1.56
S-6	6.79 \pm 0.196	11.32 \pm 0.72	7.21 \pm 0.606	5.21 \pm 0.15	107.2 \pm 2.59	6.795 \pm 0.375	21.14 \pm 1.443	1,470 \pm 10.39	74.15 \pm 3.12
S-7	9.64 \pm 0.618	13.01 \pm 1.06	11.3 \pm 1.06	4.14 \pm 0.32	114.7 \pm 1.96	10.93 \pm 1.44	30.14 \pm 1.732	1,136 \pm 6.93	65.34 \pm 2.02
S-8	7.21 \pm 0.491	38.34 \pm 1.35	26.53 \pm 1.24	8.94 \pm 0.583	105.3 \pm 3.86	23.02 \pm 2.021	87.48 \pm 2.771	2,255 \pm 5.77	165.28 \pm 4.33
S-9	3.32 \pm 0.427	17.79 \pm 0.889	10.78 \pm 0.84	6.34 \pm 0.491	76.7 \pm 1.50	6.715 \pm 0.710	51.42 \pm 1.415	1,722 \pm 7.504	101.24 \pm 6.722
S-10	3.64 \pm 0.185	9.85 \pm 0.722	8.39 \pm 0.45	5.59 \pm 0.260	77.28 \pm 2.19	5.247 \pm 0.837	41.28 \pm 0.854	1,769 \pm 9.81	88.36 \pm 1.53
Mean	7.44	15.22	11.51	4.81	93.28	8.60	45.74	1,505	93.47
LSD ($\alpha = 0.05$)	2.0	3.042	2.61	1.12	7.307	2.823	4.96	25.09	7.64
BS	2.96 \pm 0.56	4.57 \pm 0.83	5.14 \pm 0.70	1.02 \pm 0.24	45.65 \pm 5.22	2.34 \pm 0.36	10.75 \pm 1.32	763.33 \pm 30.55	32.99 \pm 6.32

Note: BDL, below detection limit (BDL); \pm indicate the standard error mean (SEM), least standard deviation (LSD) and Background Sample (BS).

Table 3 | Bioavailable, non-bioavailable and total metal concentrations in bed sediment

Metals	Parameters	% Bio-available	% Non-bioavailable	Total metal concentrations ($\mu\text{g/g}$)
Cd	Min	54.41	14.44	1.91
	Max	85.56	45.59	9.53
	Mean	73.02	26.98	5.01
	SD	10.10	10.10	2.58
Pb	Min	32.14	23.52	10.16
	Max	76.48	67.86	26.09
	Mean	53.34	46.36	18.69
	SD	15.04	15.04	6.27
Cr	Min	5.44	86.89	9.61
	Max	13.11	94.56	17.58
	Mean	8.67	91.33	13.46
	SD	2.40	2.40	2.95
Co	Min	15.35	75.26	3.48
	Max	24.74	84.65	8.86
	Mean	21.10	78.90	5.51
	SD	3.00	3.00	1.50
Mn	Min	13.13	70.37	105.13
	Max	29.63	86.87	321.03
	Mean	22.48	77.52	209.08
	SD	4.81	4.81	76.27
Ni	Min	20.57	55.08	15.32
	Max	44.92	79.43	40.66
	Mean	30.53	69.43	25.86
	SD	8.68	8.68	8.70
Cu	Min	3.85	91.21	7.48
	Max	8.79	96.15	49.88
	Mean	6.18	93.82	22.88
	SD	1.70	1.70	11.91
Fe	Min	0.81	97.90	592.77
	Max	2.10	99.19	1,240.8
	Mean	1.23	98.77	989.02
	SD	0.40	0.40	267.24
Zn	Min	9.87	78.15	30.77
	Max	21.85	90.13	101.3
	Mean	16.72	83.28	59.04
	SD	3.65	3.65	20.78

> residual > carbonate > organic. Bioavailable forms of Pb in bed sediment ranged from 32.14% to 76.48%, while non-available forms ranged from 23.52% to 67.86% (Figure 2(a)–2(e)).

Cr was available predominantly in residual bound form (67.39%), which significantly decreased in the different fraction like Fe/Mn oxide (20.79%), carbonate (5.29%), exchangeable (3.38%) and organic matter phase (3.15%), respectively. Thus, the sequential fraction of Cr in the bed sediments was bound to a different phase in the sequence as residual > Fe-Mn oxide > carbonate > exchangeable > organic. Bioavailable forms of Cr in bed sediment ranged from 5.44 to 13.11% while non-available forms ranged from 23.52 to 67.86% (Figure 2(a)–2(e)).

Co was found in residual bound from (31.65%), which further decreased as organic matter bound (25.04%), Fe/Mn oxide (22.21%), carbonate (11.94%) and exchangeable bound (9.17%), respectively. Thus, the sequential fraction of Co in the bed sediments was bound to a different phase in the sequence as residual > organic > Fe/Mn oxide > carbonate > exchangeable. Bioavailable forms of Co in bed sediments ranged from 15.35 to 24.74% (21.1%) while non-available forms ranged from 75.26 to 84.65%.

Mn was found maximum in residual bound form (44.51%), which significantly decreased as Fe/Mn oxide (29.92%), carbonate (11.45%), exchangeable (11.04%) and organic matter bound (3.09%), respectively (Figure 2(a)–2(e)). Thus, the sequential

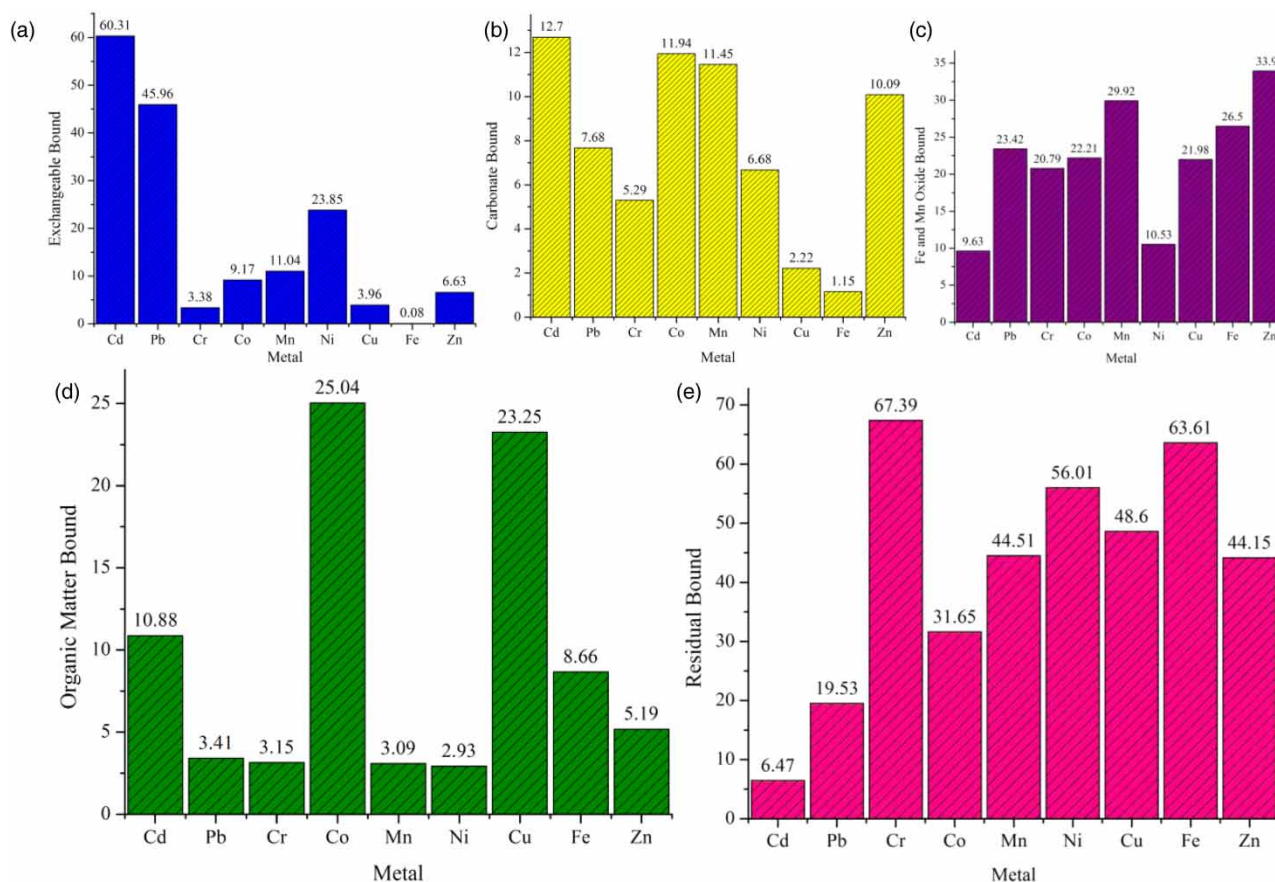


Figure 2 | Distribution percentage (a, b, c, d and e) of heavy metals for particular fractions in bed sediment of river Gomti.

fraction of Mn in the bed sediments was bound to the various phases in the sequence residual > Fe/Mn oxide > carbonate > exchangeable > organic. Bioavailable forms of Mn in bed sediment ranged from 13.13 to 29.63% while non-available forms ranged from 70.37 to 86.87%.

Ni was found in residual bound form (56.01%), which further followed a decreasing trend like exchangeable (23.85%), Fe/Mn oxide (10.53%), carbonate (6.68%) and organic matter (2.93%) bound, respectively. Following is the sequential fraction of Ni in the bed sediments in the sequence as residual > exchangeable > Fe/Mn oxide > carbonate > organic. Bioavailable forms of Ni in bed sediment ranged from 20.56 to 44.92%, while non-available forms ranged from 55.08 to 79.43%.

Highest amount of Cu was found in residual bound form (48.60%), which significantly decreased in the order as organic matter (23.25%), Fe/Mn oxide (21.98%), exchangeable (3.96%), carbonate bound (2.22%), respectively (Figure 2(a)–2(e)). Following is the sequence residual > organic > Fe/Mn oxide > exchangeable > carbonate. Bioavailable forms of Cu in bed sediment ranged from 6.18 to 8.79%, while non-available forms ranged from 91.21 to 96.15%.

Fe was found mostly in residual bound form (63.61%), which significantly decreased in the pattern as Fe/Mn oxide (26.5%), organic matter (8.66%), carbonate (1.15%) and exchangeable (0.08%) bound, respectively. The sequential fraction of Fe in the bed sediments was bound to a different phase in the sequence as residual > Fe/Mn oxide > organic > carbonate > exchangeable. Bioavailable form of Fe in bed sediment ranged from 0.81 to 2.10%, while non-available form ranged from 97.90 to 99.19%. The total Fe concentration in sediment was 989.02 $\mu\text{g/g}$, while background concentration of Fe was observed as 763.0 $\mu\text{g/g}$.

Zn showed the maximum in residual bound (44.15%) which was significantly decreased in the different fraction like Fe/Mn oxide (33.95%), carbonate (10.09%), exchangeable (6.63%) and organic matter (5.19%) bound, respectively (Figure 2(a)–2(e)). The sequential fraction of Zn in the bed sediments was bound to a different phase in the sequence of residual > Fe/Mn oxide > carbonate > exchangeable > organic. Bioavailable form of Zn in bed sediment ranged 9.87–21.85% while non-available forms 78.15 to 90.13%.

The average percentages of exchangeable metals were observed in exchangeable phase. Thus, Cd and Pb were maximum in exchangeable bound while Cr, Ni, Co, Mn Cu and Fe in residual bound. Heavy metals in both exchangeable (F-1) and carbonate (F-2) fractions of sediment were found to be relatively mobile and readily available for biological uptake, a process facilitated by the low pH. Jokinen *et al.* (2020) have also found that the similar observation for the uptake of heavy metals. In the exchangeable phase, the level of trace metals increased through the ion exchange process. This proportion is considered to be one, which constitutes the immediate nutrient reservoir for the aquatic organism. The fractions of these metals are considered to be bioavailable for aquatic as well as other life forms.

Ni, Cd, Cr and Pb have a special affinity with carbonate and may co-precipitate with carbonate minerals at high pH (Ugwu & Igbokwe 2019). The residual fraction of trace metals in this form are not soluble as tightly bound under experimental conditions. The greater the percentage contribution of the heavy metal, the smaller the pollution zone (Masindi & Muedi 2018). In this, Cu and Zn are considered as a toxic element and found to be very rare but they are insoluble. The metals in the residual fraction are usually retained within the crystal lattice of minerals and in well crystallized oxide and are thus considered to be immobile (Namur & Humphreys 2018).

The lowest percentage of bioavailable forms was found in the case of Fe and highest for Cd in sediment samples. Cd (31.3–81.2%), Cr (3.84–51.5%) and Co (18.2–65%) were also found in the non-residual fraction. In the sediment samples, the lowest percentage of non-bioavailable form was found for Cd and highest percentage for Fe. Kumar *et al.* (2020) have also found that the non-bioavailable form was found to be highest for Fe, which is the similar to the present study.

3.4. Results of factor analysis/principal component analysis

Eigen values are normally used to define the number of principal components or Factors that can be taken for further study. The first two principal components have Eigen values greater than or close to unity and explain 80.487% of the total variances of evidence contained in the original dataset for trace metals. According to Hakanson (1980), the Cd values range from 40.53 to 1598.44, which indicate a very high contamination degree of sediments.

Table 4 shows the rotated component matrix and component score for different metals in factors analysis of bed sediment in the river.

Factor 1: With an Eigen value of 5.51 and 49.58% of the variance, it has high loadings on Mn, Ni, Fe, Co and Cr, low loadings with Cu, Zn, Pb and Cd.

Factor 2: It explains 49.58% of the variance, Eigen value of 5.51, and has high loadings on Zn, and Cu, moderate loadings with Cu and low loadings on Zn, Pb and Cd (Table 4).

Principal component analysis shows the total variance for metals of bed sediment of the river, as shown in Table 5.

3.5. Hierarchical cluster analysis

Hierarchical cluster analysis was performed using Ward's method with squared Euclidean distance as the similarity measure provided a visually meaningful dendrogram. In this study, trace metals were divided into two major clusters, Fe in cluster 1

Table 4 | Rotated component matrix and component score for bed sediment

Rotated component matrix			Component score	
Metals	Factor 1	Factor 2	Factor 1	Factor 2
Zn	0.202	0.843	-0.082	0.341
Fe	0.927	0.131	0.243	-0.095
Mn	0.973	0.091	0.263	-0.121
Pb	0.101	0.729	-0.092	0.307
Ni	0.943	0.208	0.235	-0.064
Cd	0.101	0.756	-0.096	0.319
Cr	0.855	0.374	0.182	0.025
Co	0.898	0.285	0.209	-0.022
Cu	0.412	0.876	-0.027	0.321

Extraction method: Varimax with Kaiser Normalization, Rotation converged in 3 iterations.

Table 5 | Total variance explained for metals of bed sediment of river

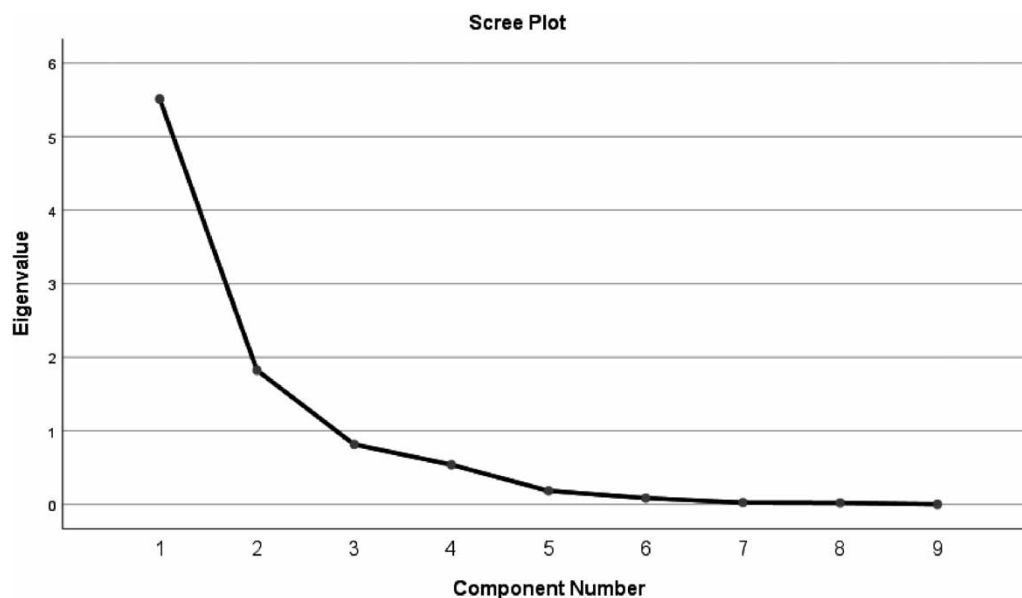
Component	Initial Eigen values of squared Loadings			Extraction sums of squared loadings			Rotation sums		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.511	61.232	61.232	5.511	61.232	61.232	4.462	49.582	49.582
2	1.823	20.255	81.487	1.823	20.255	81.487	2.871	31.905	81.487
3	0.815	9.056	90.543						
4	0.539	5.987	96.530						
5	0.184	2.039	98.569						
6	0.085	0.944	99.513						
7	0.024	0.261	99.774						
8	0.019	0.216	99.990						
9	0.001	0.010	100.000						

Extraction method: Principal component analysis.

and Zn, Mn, Pb, Ni, Cd, Cr, Co and Cu in cluster 2, further cluster 2 was subdivided into three sub clusters made with Zn in cluster 2 (1) and Mn in cluster 2 (2) and Pb, Ni, Cd, Cr, Co and Cu in cluster 2 (3). Figure 3 shows the Scree plot for total metals in bed sediment between metal components and Eigen value. The dendrograms of hierarchical cluster analysis showed the cluster of variables for total metal in bed sediment (Figure 4). Results revealed the presence of a high concentration of Cd, Pb and Zn due to anthropogenic sources and the water was classified as category V, whereas the presence of heavy metals at other sites was due to mine waste, which eroded from the river banks and was classified as II to III categories water (Ferati *et al.* 2015).

3.6. Geo-accumulation index (I_{geo}) and mobility factor of metals

The possible environmental and ecological impacts of heavy metals in the sediments were assessed through the calculated risk factors such as geo-accumulation index (I_{geo}), mobility factor (MF) of metals and risk assessment code (RAC) to find the status of pollutants risk in bed sediment. The result indicated that geo-accumulation index (I_{geo}) was observed as maximum for Cd (2.30) and Cu (2.27), which was more than 2, indicating moderate to strong pollution, whereas Pb (1.82), Zn (1.75), Co (1.52), Mn (1.44), Ni (1.44), Fe (1.40) and Cr (1.10) ranged from 1.0 to 2.0, suggesting moderate pollution of the

**Figure 3** | Scree plot for total metals in bed sediment.

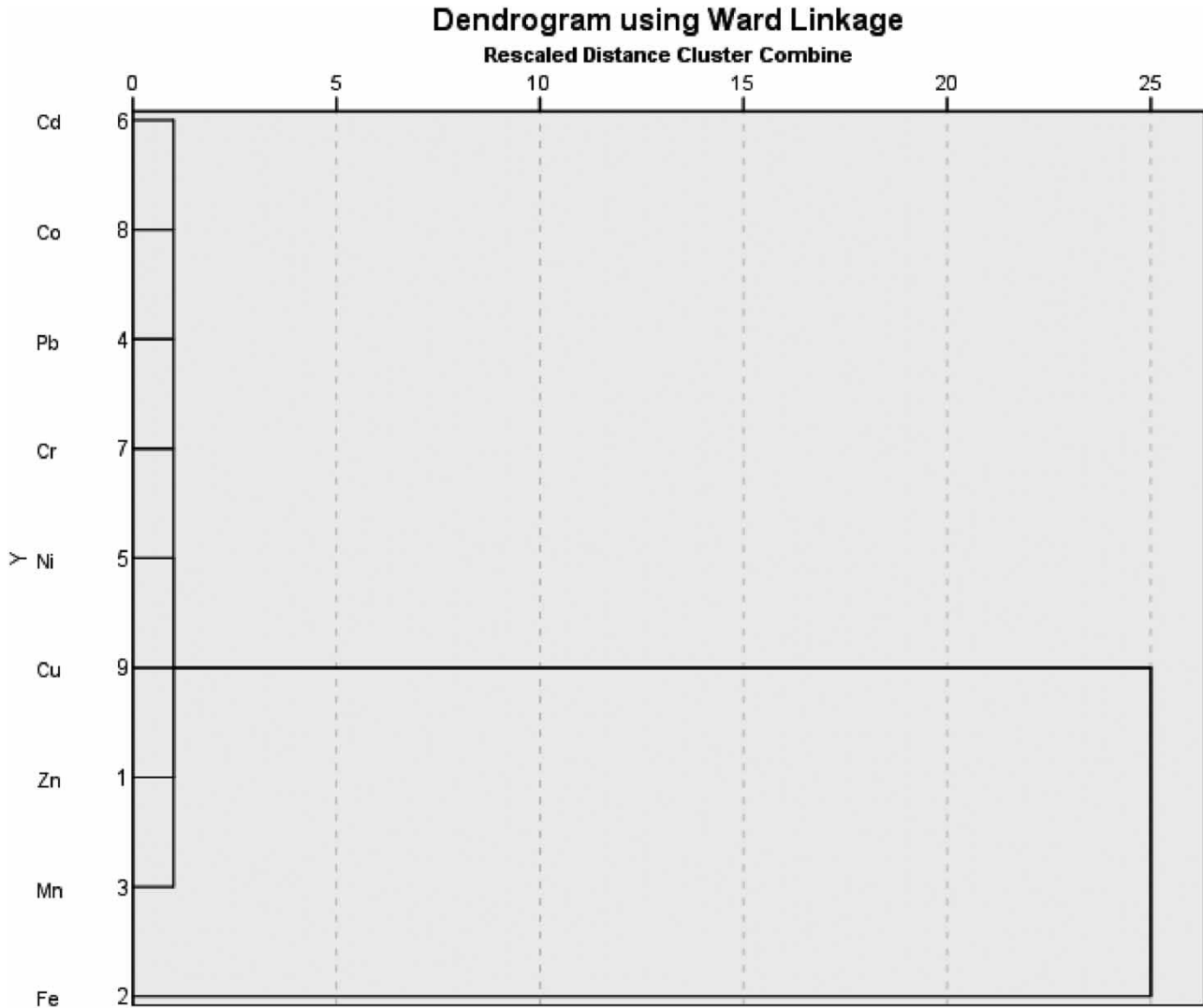


Figure 4 | Dendrograms of hierarchical cluster analysis showing the cluster of variables for total metal in bed sediment.

bed sediments (Figure 5(a)). Guan *et al.* (2018) also found that geo-accumulation index of Cd and Cu was more than 2 indicating strong pollution.

The distribution of metals in different phases, using the BCR procedure, offers an indication of their availability, which in turn reflects the risk associated with the presence of metals in the aquatic environment (Guan *et al.* 2018). Geo-accumulation index (I_{geo}), a widely used practical relationship for evaluating the quantity of metal contamination or pollution in soil or sediment samples of terrestrial or aquatic environments, was applied to evaluate the pollution status of the studied area (Muller 1979).

Mobility factors were observed for different heavy metals in bed sediments of the river which ranged from 0.012 to 3.192. The maximum mobility factor was observed for Cd (3.192) and minimum for Fe (0.012). The decreasing order of mobility factor was observed as Cd > Pb > Ni > Mn > Co > Zn > Cr > Cu > Fe (Figure 5(b)).

3.7. Risk Assessment Code (RAC)

The result showed that risk assessment code of Cd and Ni ranged from 54.41 to 85.56 and 20.57 to 44.92, respectively, which were under very high risk while the risk assessment code of Pb varied from 32.14 to 76.48, which was found to be at high risk. Zn (9.87–21.85) and Co (15.35–24.74) were at medium risk, while the Cr (5.44–13.11), Mn (13.13–29.63), Cu (3.85–8.79) and Fe (0.81–2.10) were found at low risk. The risk assessment code gives an indication of the possible risk by applying a scale to

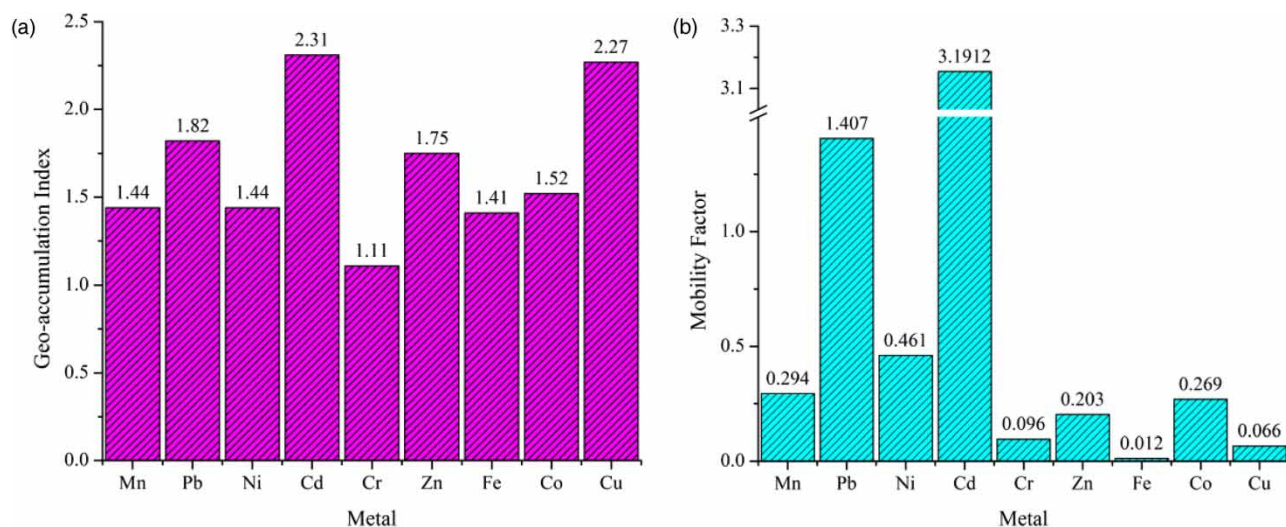


Figure 5 | Geo-accumulation index (I_{geo}) (a) and mobility factor of metals (b) of heavy metals for particular fractions in bed sediment of river Gomti.

the percentage of metals present in the exchangeable and carbonate fractions. Accordingly, if this value is $<1\%$ there is no risk for the aquatic system; 1–10% indicates low risk, 11–30% medium risk, 31–50% high risk, and $>50\%$ very high risk (Jain 2004; Singh *et al.* 2005).

The lowest mobility factor was found for Fe and highest for Cd. The lowest risk assessment code values were low risk for the Mn, Fe, Cr and Cu, while the highest risk assessment code values were for the Pb and Cd. Other metals were found to be of medium risk. Zn, Mg and Co was very high risk. Risk assessment code revealed that more than 50% of Cd is in exchangeable or carbonate-bound fractions as reported by Al-Mur (2020) and therefore comes under the very high risk category and can easily enter the food chain because of the toxicity, mobility and availability of Cd. It can pose serious problems to the aquatic ecosystem.

4. CONCLUSIONS

The geochemical variations and distribution patterns of selected metals are very instructive in the sediments of Gomti River. Among the metals, Cr, Cu, Mn, Ni, Fe and Zn were distributed mainly in the residual fraction while Pb was in carbonate fractions. Risk assessment code and I_{geo} factors in the sediments showed medium risk for Cr, Cu, Mn, Ni, Mg, Fe; high risks for Zn and very high risks for Cd and Pb. Mobility factors were in the order of $Cd > Pb$, preferentially associated with the bioavailable fractions and could be used as indicators for contribution from the anthropogenic sources, while Cr, Co, Mn, Ni, Cu, Fe and Zn were associated to a greater extent with the residual fraction, indicative of natural origins. Overall Cd, Pb, Ni and Cr emerged as major pollutants in the sediments in the mid-stream of the river, which were in insecure proximity to densely populated urban/semi-urban locality, where diverse anthropogenic activities contributed to the majority of the hazardous pollutants in the study area.

CONSENT FOR PUBLICATION

Not applicable.

COMPETING INTERESTS

The authors declare that they have no competing interests in this section.

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AUTHORS' CONTRIBUTIONS

The main investigator was Vinay Kumar, who designed the manuscript. The technical drafting of the manuscript was done by Markandeya, while Pokhraj Sahu helped in writing. All the authors have read and approved the manuscript.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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