

Geochemical and environmental risk assessment of hazardous elements in river sediment

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Abstract The peninsular river Damodar is the life line of eastern India, facing critical pollution problems due to sewage, industrial waste disposal as well as coal mining along the river valley. Sediment samples were collected and analyzed for various geochemical phases of hazardous elements, and associated environmental risks were evaluated. This paper provides chemical fractionation of nine (Cd, Mn, Zn, Ni, Cu, Pb, Co, Cr, Fe) elements from river sediment by using Tessier five step sequential extraction method. The study was aimed (1) to understand dynamics and mobility of elements in different geochemical fractions; (2) to evaluate bioavailability and ecological risk of these elements by RAC; and (3) to identify contaminated and uncontaminated sites by using cluster analysis. The result of the study revealed maximum bioavailable fraction was that of Cd. Bioavailable elements in studied sediment followed the order Cd (23.76%) > Mn (14.19%) > Zn (13.54%) > Ni (12.82%) > Cu (7.12%) > Pb (7.05%) > Co (6.09%) > Fe (4.98%) > Cr (2.03%). Maximum % of the reducible fraction was found for Fe (14.38%) while in organic fraction Cu (11.25%) was maximum. Residual fraction dominates in all elements with a maximum percentage of 83.85% for Co. Risk assessment by RAC reveals that the river was under medium risk due to Cd, Mn, Zn and Ni while at low risk for rest of the elements. Cluster analysis shows that three sampling sites were highly contaminated,

three were moderately contaminated and six were contaminated while only one site was uncontaminated.

Keywords Hazardous element · Cadmium · Speciation · Sediment · Geochemical · Ecological risk

Introduction

Sediment is an inseparable part of any river system as it provides nutrients for living organisms and acts as a sink for elements (Akçay et al. 2003). Hazardous elements are common and significant pollutants to the soil, river system and air flowing through an industrial areas (Rodríguez-Iruretagoiena et al. 2016; Civeira et al. 2016a, b; Agudelo-Castañeda et al. 2016; Schneider et al. 2016; Saikia et al. 2016; Sehn et al. 2016; Dalmora et al. 2016). The ecological toxicity of elements is well known due to its persistence and non-biodegradable nature (Louma 1983; De Souza et al. 1986; Lacerda et al. 1992; Allen and Hansen 1996). Hazardous elements can be introduced into rivers and another aquatic environment by natural processes such as chemical leaching of bedrocks in the drainage basin. Moreover, anthropogenic activities such as discharge of urban runoff, domestic and industrial wastewater, mining and smelting operations, combustion of fossil fuels, processing and manufacturing industries etc. also add pollutants to the river system in a massive way (Wang and Morrison 2014; Saikia et al. 2015; Sanchís et al. 2015; Tezza et al. 2015; Wilcox et al. 2015; Sindelar et al. 2015). Elements are present in different geochemical forms in an aquatic system, have various physical and chemical behaviors in terms of chemical interaction, mobility, and potential toxicity (Akçay et al. 2003; Singh et al. 2005b). Biogeochemical and eco-toxicological consequences of

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elements in bottom sediment are determined by their concentration in specific phases or chemical species (speciation of elements) but not on the total metal content (Shrivastava and Banerjee 2004). Most of the previous studies hovered around the estimation of total metal concentration in sediment to evaluate the potential impact on the aquatic environment. Generally, the total metal concentration is evaluated by one step strong acid digestion of the sediment. Evaluation of total metal concentration is the basis for evaluation of global index of contamination, but it does not evaluate the potential toxicity of hazardous elements. The total element studies also do not give information about bioavailability and mobility of elements in the sediment (Mc Bride 1995; Shrivastava and Banerjee 2004). Tessier et al. (1979) first proposed the complete sequence of element fractionation by sequential extraction. Later on various researchers worked on speciation of elements in sediment such as Singh and Hasnain (1999), Lee et al. (2000), Morillo et al. (2002), Violante et al. (2010), Simpson et al. (2012), Zhang et al. (2014), Zhuang and Gao (2014), Ladigbolu et al. (2014), Saleem et al. (2015), Taberna et al. (2015), Venkatramanan et al. (2015). The elements were found to be present in five different chemical forms: exchangeable, bound to carbonate, bound to Fe–Mn (reducible), organic fraction, and residual (Morillo et al. 2002). The exchangeable fraction consists of weak bond elements adsorbed on sediment surfaces and readily equilibrate with aqueous water phase after a slight change in the ionic composition of water. The carbonate fraction may get released back to water phase after a slight change in pH (generally in acidic pH) (Zerbe et al. 1999). The elements present in exchangeable and carbonate fractions are readily bioavailable and considered as a basis for estimation of element toxicity of sediment by RAC method. The Fe–Mn (reducible phase) bound elements are sensitive to redox potential and unstable in anaerobic condition. The organic fraction is temporarily unavailable but may get released back to water due to digestion and decomposition by microbes. The residual fraction is elements in the crystal lattice of minerals like silicates. Elements of this fraction are non-bioavailable and generally belong to the natural origin (Zerbe et al. 1999). The present study has been conducted on Damodar River flowing in eastern India which is also a tributary of the holy river Ganges. It passes through a number of coalfields and allied industrial clusters. The river also meanders through a number of user townships, villages and agricultural land. Various studies on the Damodar river water were conducted by researchers but very few considered speciation of elements in its sediment for example, Singh et al. (2014), Haldar et al. (2016), Verma et al. (2012), Gupta and Banerjee (2012), Ghosh and Banerjee (2012), Chatterjee et al. (2010) worked on water quality while Singh et al.

(2005b), Singh and Hasnain (1999), Singh et al. (1999) worked on river sediment.

Materials and methods

Materials

The reagents sodium acetate (NaOAc), ammonium acetate (NH_4OAc , 98%), perchloric acid (HClO_4 , 70%) were from Sigma Aldrich and acetic acid (HOAc , 25%v/v), hydrogen peroxide (H_2O_2 , 30%), hydrofluoric acid (HF, 40%), hydrochloric acid (HCl, 35%), nitric acid (HNO_3 , 69%), were from Merck, and hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was from Tokyo chemical industry corporation limited, Tokyo, Japan were used. These reagents were of analytical grade and used without any further purification. All the glass-wares (Borosil, India) used for the experiments were cleaned by 10% v/v HNO_3 and rinsed with deionized water (resistivity $\geq 18 \text{ M}\Omega\text{-cm}$) prior to use.

Methods

Study area

The middle stretch of Damodar River covering a length of 57 km was considered for the study. The Tenughat Dam ($23^\circ44'06''\text{N}$, $85^\circ48'36''\text{E}$) lies on the upstream of study area, and the terminal point ($23^\circ43'05.77''\text{N}$, $86^\circ11'56.62''\text{E}$) was the confluence of an important tributary rivulet called Garga. The river has three tributaries Konar (S4), Jamunia (S11) and the Garga (S12) within this stretch. The area is mushroomed with coal mining and allied industries such as coal washery, thermal power plants, steel plants, and cement industries. Important townships such as Bokaro steel city, Bokaro thermal city, many populated villages and agricultural plots are also present within the study area. Map of the study area with sampling location is presented in Fig. 1.

Sample collection and preparation

Total 13 sampling points were strategically selected for sampling and analysis of element speciation in the river sediment. Sampling sites were selected according to varying anthropogenic activities along river basin and confluence of its tributaries (Fig. 1). A composite sampling of top 2 cm sediment was done by using grab sampler and simple scoop method. Collected samples were dried at room temperature and sieved with 75 μm sieve. The sediment samples having a size less than 75 μm were used for sequential extraction of elements (Ni, Pb, Cr, Co, Cd, Zn,

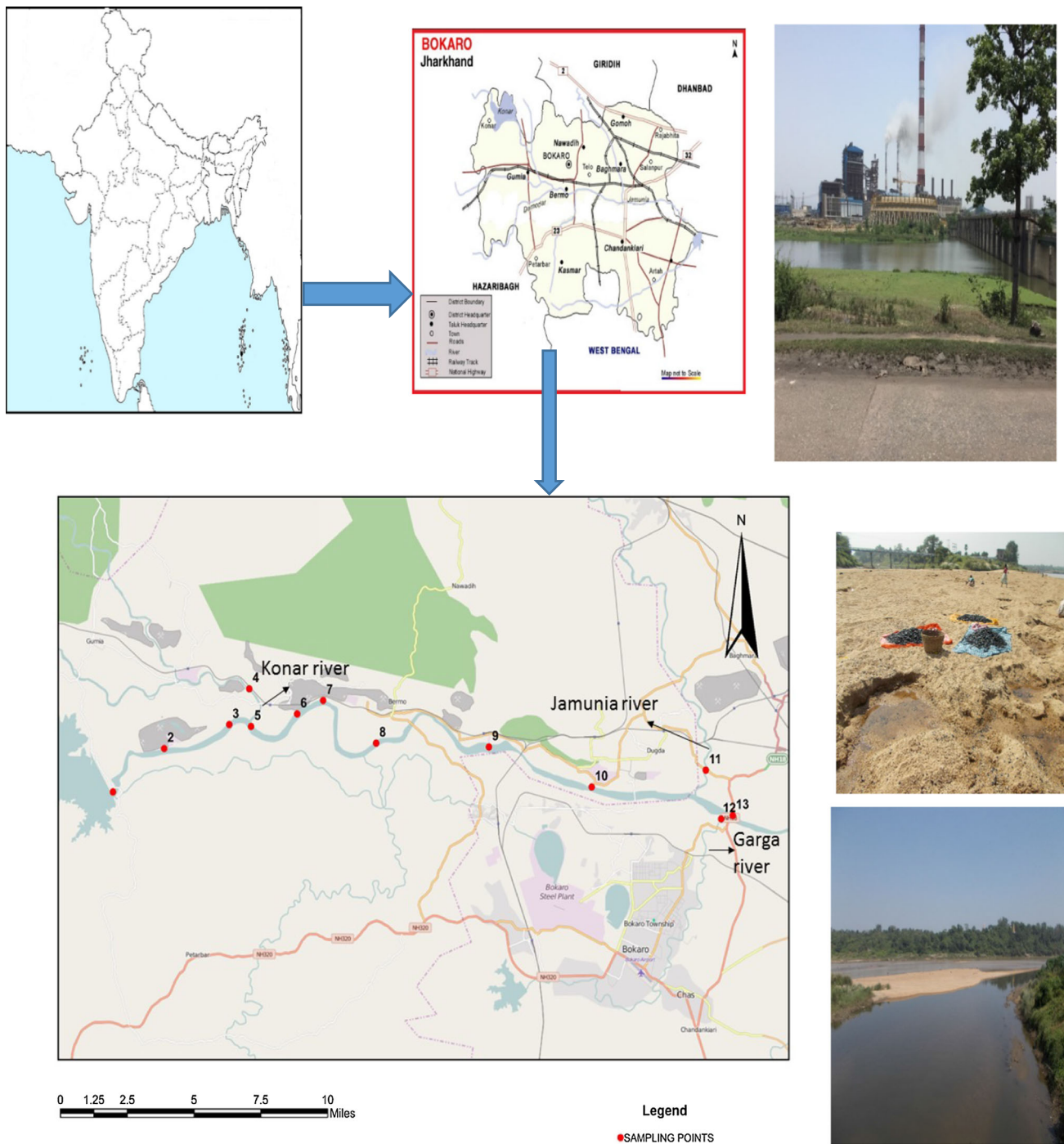


Fig. 1 Showing map of study area with sampling locations

Mn, Cu and Fe). Fractionation of elements was conducted by well-known five step sequential extraction method developed by Tessier et al. (1979) to get exchangeable (step I), carbonate bound (step II), Fe–Mn bound (step III), organic bound (step IV) and residual fraction (step V), respectively. The same fractionation method for elements was also followed by various researchers in recent years

(Sundaray et al. 2011; Anderi et al. 2015; Jain 2004; Singh et al. 2005a). The exchangeable fraction was fractionated by continuous agitation of 1 gm prepared sediment sample with NaOAc at pH 8.2 for 1 h at room temperature in 50 ml polyethylene centrifuge tube. The supernatant was obtained after centrifuge (REMI-24, Mumbai, India) at 2000 rpm for 30 min with the help of micropipette. The

Table 1 Metals concentration in standard reference material (Estuarine sediment NIST—1646a)

Element	Certified concentration (mg/kg)	Observed concentration (mg/kg)	Recovery (%)
Ni	23	23.7 ± 4.04	103.04
Pb	11.7	12.7 ± 1.53	91.45
Cr	40.9	36.6 ± 1.20	89.5
Co	5	5.56 ± 0.42	111.2
Cd	0.148	0.135 ± 0.005	91.22
Zn	48.9	51.7 ± 4.70	105.7
Mn	234.5	227.7 ± 2.50	97.1
Cu	10.01	9.5 ± 1.46	94
Fe	20,080	20909 ± 36.60	104.13

residue from step I was continuously agitated for 5 h with 8 ml 1 M NaOAc at pH 5 adjusted with HOAc. Again, it was centrifuged for 30 min at 2000 rpm and the supernatant was separated to get carbonate bound elements. The residue from step II was continuously agitated for 4 h at 96 ± 3 °C with 20 ml 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% v/v HOAc. The supernatant was separated after centrifuge to get Fe–Mn bound fraction. The residue from step III was heated for 2 h with occasional agitation with 3 ml 0.02 M HNO_3 and 30% H_2O_2 at pH 2 (adjusted with HNO_3) and left for cooling. Again 3 ml 30% H_2O_2 was added and heated at 85 ± 2 °C for 3 h with occasional agitation and left for cooling. Then, 5 ml 3.2 M NH_4OAc in 20% v/v HNO_3 was added and the volume was make up to 20 ml and agitated for 30 min. After that, it was subjected for centrifuge at 2000 rpm for 30 min and the supernatant was separated to get organic bound elements in the sediment. The residue from step IV was digested in the platinum crucible on a hot plate with 2 ml HClO_4 and 10 ml HF to near dryness. Again 1 ml HClO_4 and 10 ml HF was added and evaporated to near dryness. Then, 1 ml HClO_4 was added and evaporated till white fumes appear. The residue was dissolved in 12 N HCl and diluted to 25 ml. The supernatants from all the steps and final digested sample were filtered through Whatman #42 filter paper. Filtered samples were analyzed through flame atomic absorption spectrophotometer (FAAS) (FAAS- GBC Scientific Avanta, Australia). Analytical grade chemicals were used to prepare relevant blanks, and calibration curves were made. All the experiments were done in the department of Environmental Science and Engineering, Indian Institute of Technology (Indian School of Mines) Dhanbad, Jharkhand, India. Similar analytical procedures were previously reported (Dias et al. 2014; Saikia et al. 2014; Cutruoneo et al. 2014; Oliveira et al. 2014; Martinello et al. 2014; Arenas-Lago et al. 2014; Silva et al. 2014; Garcia et al. 2014; Pérez et al. 2014). The analytical method was validated by NIST-1646a standard reference material (Estuarine sediment) delivered by National Institute of Standards and Technology (NIST), USA. The accuracy and precision

were checked by reference material under same environmental condition. The recovery % varies between 89.5 and 111.2 (Table 1).

Result and discussion

Geochemical speciation of Ni, Pb, Cr, Co, Cd, Zn, Mn, Cu and Fe in surficial sediment at different sampling stations in middle stretch of the Damodar river is presented in percentage graph, Fig. 2a–i. Range and mean of these elements in different geochemical fractions are presented in Table 2. Each geochemical form has different behavior with changing environmental condition of the aquatic system. The elements associated with different chemical fractions in Damodar River and its tributaries, Konar River (S4), Jamunia River (S11) and Garga River (S12) follow the order as given below:

Ni—Residual > Reducible > Organic > Carbonate > Exchangeable
 Pb—Residual > Reducible > Organic > Carbonate > Exchangeable
 Cr—Residual > Reducible > Organic > Carbonate > Exchangeable
 Co—Residual > Reducible > Organic > Carbonate > Exchangeable
 Cd—Residual > Carbonate > Exchangeable > Reducible > Organic
 Zn—Residual > Reducible > Carbonate > Organic > Exchangeable
 Mn—Residual > Reducible > Carbonate > Exchangeable > Organic
 Cu—Residual > Organic > Reducible > Carbonate > Exchangeable
 Fe—Residual > Reducible > Organic > Exchangeable > Carbonate

A similar pattern of element speciation was found by Sundaray et al. (2011) in Mahanadi river sediment, India. The Cd speciation was totally different from other elements

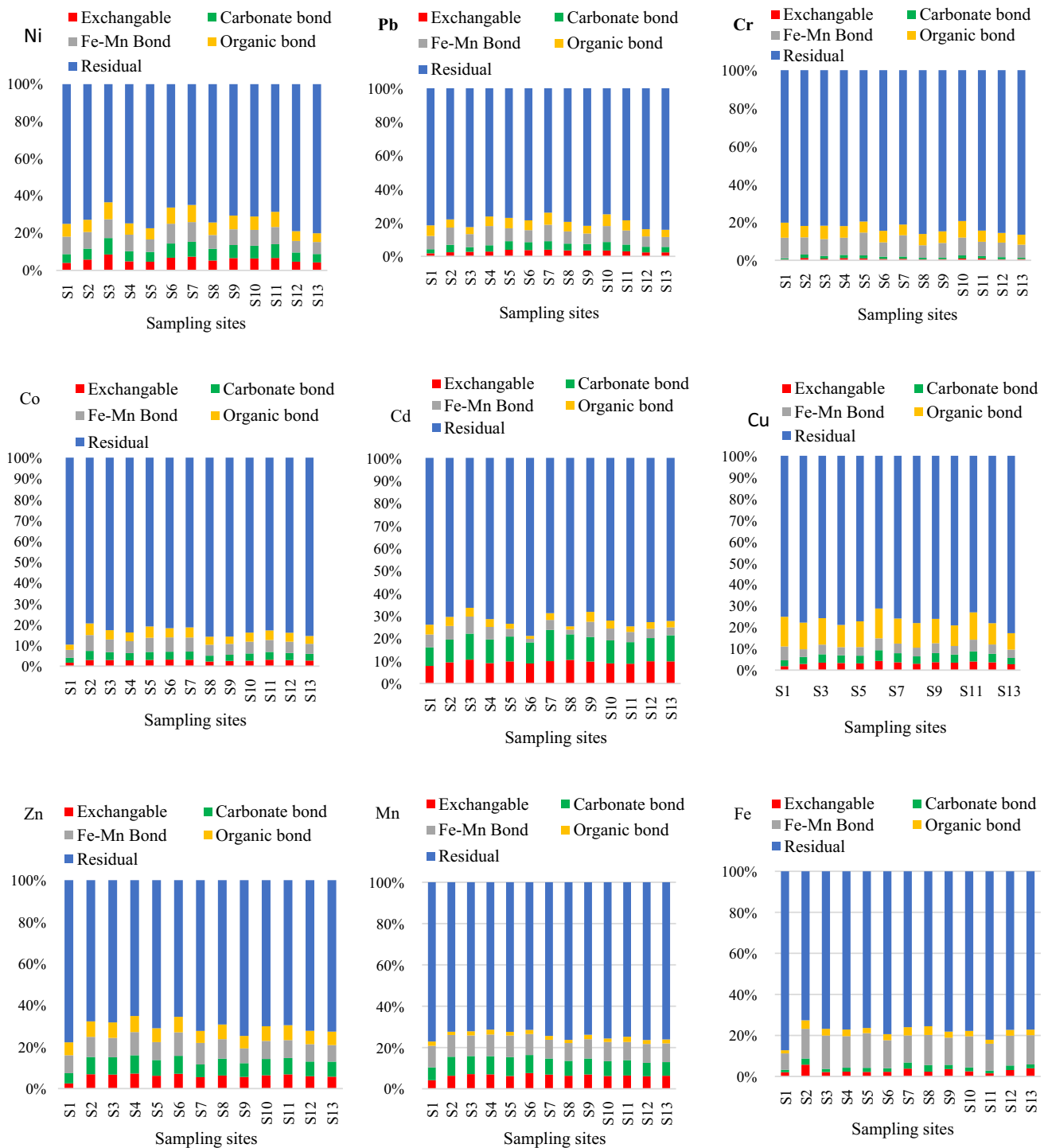


Fig. 2 Hazardous element speciation at different sites in Damodar River sediment

under study. Mostly, it was bond with first three fractions (24.42%), i.e., exchangeable (9.6%), carbonate (10.35%) and Fe–Mn (4.45%), the result was concurrent with Yamuna river sediment, Mahanadi river sediment in India and Lake Naivasha, in Kenya (Jain 2004; Sundaray et al. 2011; Njeng et al. 2009). Ni, Pb, Cr, and Co follows a similar pattern of geochemical speciation in the Damodar river sediment.

Exchangeable fraction

Exchangeable fractions are loosely bound elements of anthropogenic origin; therefore, its high concentration in sediment indicates pollution (Singh et al. 1999). Elements of this fraction are readily available for living biota (Ladigbolu 2014) and may rapidly equilibrate with an

Table 2 Risk assessment code according to RAC guideline Kabala and Singh (2001)

Category	Risk	Metals in carbonate and exchangeable fractions (%)
1	No risk	< 1
2	Low risk	1–10
3	Medium risk	11–30
4	High risk	31–50
5	Very high risk	> 50

aqueous phase (Gibb 1977). In this study, the order of exchangeable elements were $Cd > Mn > Zn > Ni > Cu > Pb > Fe > Co > Cr$ with their % contribution of (9.5, 6.58, 5.73, 5.6, 3.3, 3.1, 2.9, 2.69, 0.83) respectively, as shown in Fig. 2. The cadmium has high (9.5%) exchangeable fraction at all sampling stations. Exchangeable Cd was also highest among studied elements due to its high capacity of principal polarization, hence hold high ecological risk. Similar result was also found in Yangtze River sediment, China (Yang et al. 2009). Exchangeable Cr was least among the studied elements at all sampling stations. Similar results were previously divulgated by other authors also (Davutluoglu et al. 2011; Morillo et al. 2002; Jain et al. 2007; Yang et al. 2009; Oliveira et al. 2013; Hower et al. 2013a, b; Arenas-Lago et al. 2013; Silva et al. 2013a, b; Kronbauer et al. 2013; Sanchís et al. 2013; Oliveira et al. 2014; Ribeiro et al. 2013a, b; Cerqueira et al. 2013; Osório et al. 2014).

Carbonate fraction

Elements that have a tendency to precipitate and co-precipitate with carbonate are easily scavenged with sediment carbonates/sulfates (Quispe et al. 2012; Silva et al. 2012a, b; Cerqueira et al. 2012; Oliveira et al. 2012). Elements like Cd, Mn, Zn, Ni, and Pb have high affinity with carbonate (Sundaray 2007). Carbonate bound elements in polluted river sediment are detrital or authigenic and its concentration may reach up to 50% (Singh and Hasnain 1999). The elements present with carbonate fraction in Damodar river sediment follow the order $Cd > Mn > Zn > Ni > Pb > Cu > Co > Fe > Cr$ with percent contribution of (10.26, 7.8, 7.46, 6.06, 3.98, 3.97, 3.5, 2.1, 1.2), respectively (Fig. 2). Carbonate bond Cd was maximum in the studied river because $CdCO_3$ can be easily formed in neutral pH but may release back to aqueous phase with a decrease in pH, this was consistent with result found by Balistrieri et al. (2007) in USA and Yang et al. (2009) in China. Carbonate Mn was second highest due to the similarity of ionic radius of Ca in $CaCO_3$, forming a

$MnCO_3$ precipitate (Rath et al. 2009; Zhang et al. 1988). Carbonate Cr was least which may be due to the inability of the Cr^{3+} ion to form a precipitate or complex with carbonates (Sundaray et al. 2011; Islam et al. 2015).

Fe–Mn oxides fraction

Oxides of Fe and Mn are good scavengers for almost all trace elements. Elements in aqueous phase get adsorbed, flocculated and co-precipitated with Fe and Mn oxy-hydroxides (Iwegbue et al. 2007; Passos et al. 2010; Venkateswaran et al. 2007; Rath et al. 2009; Bordas and Bourq 2001; Purushothaman and Chakrapani 2007). Order of Fe and Mn bond elements in Damodar river sediment are $Fe > Mn > Zn > Cr > Ni > Pb > Co > Cd > Cu$ with their percent contribution in sediment (14.38, 9.56, 9.13, 8.63, 8.08, 7.65, 5.79, 4.45, 4.34), respectively, are presented in Fig. 2. In this fraction, Fe was maximum followed by Mn because both elements form stable solid compounds with their oxide and hydroxide in the sediment. (Venkateswaran et al. 2007). There was a large difference in % of Fe and Mn in this fraction due to the high susceptibility of Mn toward reduction which results in solubilization of precipitated Mn into the aqueous phase. The solubilized Mn gets bound with exchangeable phase causing an increase in its concentration in exchangeable phase (Palleiro et al. 2016).

Organic fraction

Organic matter contributes an important role in distribution and dispersion of hazardous elements in sediment by the formation of organic ligands and metal complexes. The low molecular weight organic matter in aquatic environment produce dissolved ligands, while macromolecule reduces elements availability by adsorption on sediment containing organic ligands (Zhang et al. 2014). Organic bound elements present in various forms such as: in living organisms, detritus, coating on mineral particles etc. due to its complexation and poertization properties (Ribeiro et al. 2010; Silva et al. 2009a, b). Elements of this fraction are not readily available due to its slow rate of release hence are less toxic to the aquatic environment (Vicente-Martorell et al. 2009). Organic bound elements in studied river follow the order $Cu > Zn > Ni > Cr > Pb > Co > Fe > Cd > Mn$ with their percent contribution (11.25, 6.78, 6.56, 6.1, 5.26, 4.14, 3.05, 3, 1.94), respectively (Fig. 2). The organic bond Cu was maximum due to easy formation of organic-Cu complex with high stability (Sundaray et al. 2011). The source of Cu may be sewage which carries a large amount of organic matter associated with an oxidizable fraction (Vicente-Martorell et al. 2009). Percent contribution of Zn, Ni and Cr were almost similar

followed by Pb. The Mn was least due to its weak affinity with organic compounds (Venkatramanan et al. 2015) and competition between Fe and Mn ion to form a complex with organic compounds (Sundaray et al. 2011).

Residual fraction

Elements in this fraction are silicate bound that is strongly held within the crystal lattice, not soluble under experimental condition (Singh et al. 1999; Ladigbolu et al. 2014). Result of the study demonstrate that almost all elements dominate in this phase range from 83.85% for Co to 70.25% for Zn similar result were found by Singh et al. (1999) in Damodar river, India, Rath et al. (2009) in Brahmani and Nandira river, India, and Saleem et al. (2015) in Mangla Lake, Pakistan. Residual fraction in studied river were in the order $Co > Cr > Pb > Fe > Cu > Mn > Ni > Cd > Zn$ with their percent contribution (83.85, 83.2, 80.16, 77.65, 77.1, 74.08, 73.73, 71.8 70.48), respectively, are given in Fig. 2. Sources of residual elements in the sediment are natural; however, their concentration is controlled by mineralogy and extent of weathering of parent rock (Singh et al. 1999). In the present case, the intense opencast coal mining (Gondwana coal) on the bank of middle stretch of the river intensifies the rate of erosion of parent rock (weathering process). These get deposited into the river as sediment where their further weathering occurs. Hence, the source of residual fractions of elements in the Damodar river is anthropogenic, i.e., induced by coal mining in addition to natural.

Cluster analysis

Hierarchical agglomerative cluster analysis (CA) implemented on normalized data set of bioavailable elements by means of Ward's method and Euclidean distances as a measure of similarity (Sundaray et al. 2011). Sampling sites were grouped into the various degree of contamination such as contaminated, uncontaminated, moderately and highly contaminated according to the enrichment of bioavailable fraction in the sediment by using cluster analysis (Saleem et al. 2015; Rath et al. 2009; Cassdo-Martinez et al. 2009; Yang et al. 2009). In the present study, sampling sites were grouped into four clusters as shown in the dendrogram (Fig. 3). The sampling sites of the same group may have somewhat similar anthropogenic sources. Group 1 include highly contaminated sites (3, 6 and 7), these sites receive sewage from small townships near these stations. Site 3 receives wastes from thermal power plant. Site 6 and 7 have opencast coal mining on the bank of the river and site 7 receives agricultural waste and runoff in addition. The group 2 includes only one sampling site which was uncontaminated and has minimal

anthropogenic interference. Hence, the sources of elements at site 1 may be of lithogenic origin (Rath et al. 2009). The group 3 includes moderately contaminated sites (2, 12 and 13). Site 2 receives sewage from Kathra town and waste from ash pond of Kathra TPP as well as runoff from the agricultural field at opposite bank of the river. The S12 was Garga River, a tributary of River Damodar carries wastes from Bokaro steel plant, sewage from Bokaro Steel City, Chas Township, nearby small villages and agricultural fields. S13 was the junction point of River Garga and Damodar representing similar characteristics which show a clear effect of Garga River on Damodar. Site No. 4, 5, 8, 9, 10 and 11 were contaminated sites and under group 4. The site 4 is Konar River, having Bokaro TPP and Bokaro thermal city on its bank which meets to Damodar River at site 5 representing similar sediment characteristics. The site 11 was also a tributary (Jamuna) of River Damodar having small villages, towns, intensive coal mining and coal washery near its bank. Near site 10 there were Chandrapura thermal power plant and Chandrapura town. Near site 8 and 9 there were coal washery and small towns. Result of cluster analysis also show that almost all sampling sites except site 1 in present study are contaminated to highly contaminated due to anthropogenic sources which may be due to settlement of towns, coal mining and allied industries along the bank of the river which is concurrent with the finding of Saleem et al. (2015) in the Mangla Lake, Pakistan. Hence, suitable remediation steps such as the installation of sewage and effluent treatment plant, taking suitable steps to minimize the release of coal mining and allied industrial wastes into the river can be taken to reduce pollution in the river system.

Ecological risk assessment

The potential environmental risk of hazardous elements in sediment largely depends on its geochemical speciation (Yang et al. 2009). Exchangeable and carbonate fractions are weakly retained and may equilibrate with aqueous water phase, hence holds more ecological risk than rest of the fractions (Rath et al. 2009). The concentration of bioavailable and non-bioavailable elements in the studied river sediment is presented in Fig. 5. Risk assessment code (RAC) was used to study the risk associated with elements speciation in river sediment (Perin et al. 1985; Singh et al. 2005a; Jain 2004). Risk assessment code states the possible risk associated with element speciation in sediment by applying a scale to the elements present in exchangeable and carbonate fractions. The RAC according to its guidelines are tabulated in Table 2. RAC indicates that elements with less than 1% carbonate and exchangeable fraction are safe for the environment while more than 50% of total element concentration in these fractions will be hazardous

Fig. 3 Dendrogram showing contamination at different sampling stations

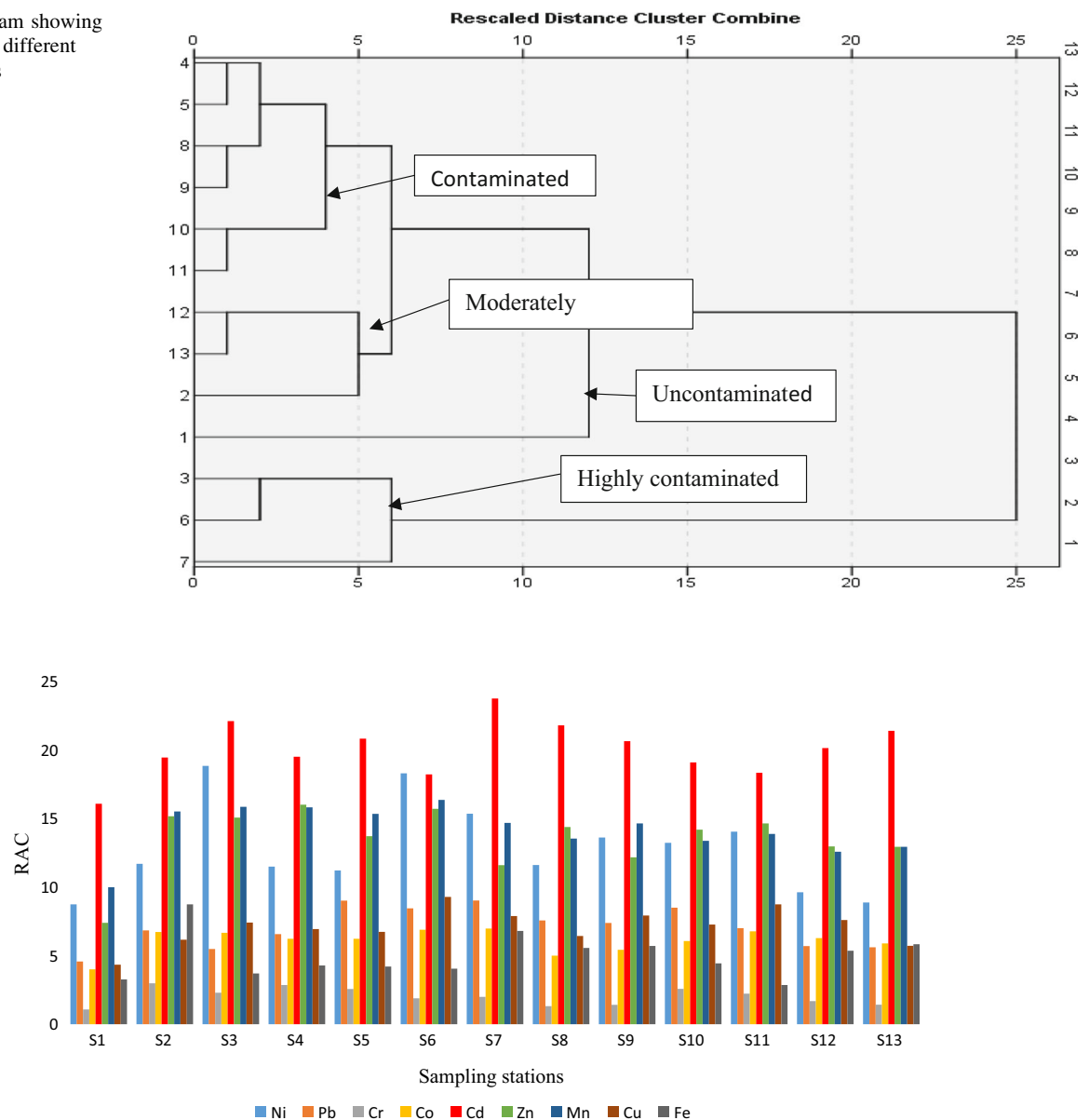


Fig. 4 RAC of hazardous elements in Damodar river sediment at different sampling stations

for the environment and can easily enter the food chain (Rath et al. 2009). Risk assessment of present study is provided in Fig. 4. It shows that the River sediment holds medium risk for Cd (23.76%), Mn (14.19%) Zn (13.54%) and Ni (12.82%) at all sampling stations with exception of Ni (low risk at S1, S12 and S13). The S1 has minimum percentage contribution of bio-available fraction for all the elements studied and were under low risk for all elements studied except Cd (16%) and Mn (10%). Cd possessed highest bio-available percentage at S7 (23.76%) followed by S2 (22.12%), maximum % of Mn was at S6 (16.36), Ni was maximum at S3 (18.85%), while Zn was maximum at S4 (16.02%). The river was at low risk for Pb (7.05%), Cu

(7.12%), Co (6.09%), Fe (4.98%), and Cr (2.03%). The RAC study of hazardous elements in present study shows that the river is at maximum risk for Cd among studied elements and minimum risk of Cr, which is similar to Chaohu lake China (Zhang et al. 2014) and Mahanadi Basin India (Sundaray et al. 2011). Overall risk analysis of elements shows that the studied river is at low to medium risk for all elements which may be due to the discharge of sewage, industrial effluent, coal mining and its allied industrial wastes into the river and intensive agriculture. These risk levels may increase in near future due to increase in industrial production, population and agriculture unless some mitigation measures are taken.

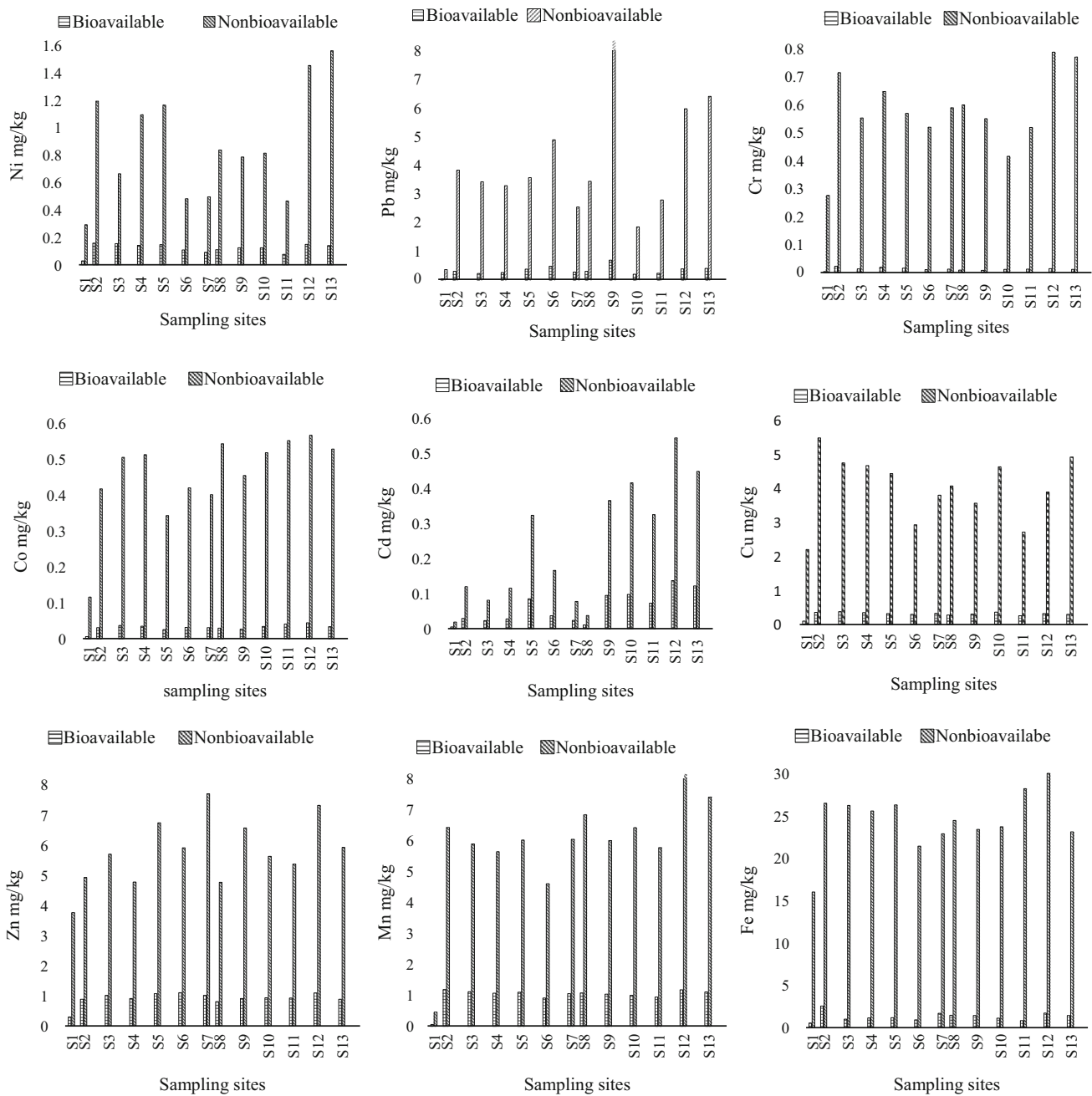


Fig. 5 Bioavailable and non-bioavailable forms of elements (mg/kg) in Damodar river sediment at different sampling stations

Conclusions

The present study suggested that the river was under medium risk for Cd, Mn, Zn and Ni while at low risk for Cu, Pb, Co, Fe, and Cr. The bioavailable fraction of Cd, Mn, Zn, and Ni was higher than other elements studied due to special affinity of these elements toward carbonates. The iron was maximum in reducible phase, while Cu was maximum in the Organic phase. The Cr concentration was minimum in exchangeable phase and Cu was minimum in

reducible, while Mn was minimum in organic fraction. The organic matter act as a good scavenger for almost all elements studied. Residual phase dominate in all elements studied, it varies from 70.48 to 83.85%. The cluster analysis confirmed that the river was highly contaminated at sampling sites 3, 6 and 7, moderately contaminated at 2, 12 and 13 and contaminated at site 4, 5, 8, 9, 10 and 11, while site 1 was uncontaminated. It can be concluded from the study that the river is contaminated with Cd, Zn, Mn, and Ni. The study also shows that anthropogenic activities

trigger the elements input into the river stream which ultimately leads to pollution. There is an urgent need to install sewage treatment plants to capture the pollutants in sewage. The mining and allied industries along with steel and cement industries should adopt stringent effluent and other industrial solid waste control and disposal measure to minimize pollutants discharge into the river.

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