

Metal fractionation study on bed sediments of River Yamuna, India

C.K. Jain

National Institute of Hydrology, Roorkee 247 667, India

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Abstract

The pollution of aquatic ecosystem by heavy metals has assumed serious proportions due to their toxicity and accumulative behavior. The toxicity and fate of the water borne metal is dependent on its chemical form and therefore quantification of the different forms of metal is more meaningful than the estimation of its total metal concentrations. In this study fractionation of metal ions on bed sediments of River Yamuna has been studied to determine the eco-toxic potential of metal ions. The investigations suggest that copper have a tendency to remain associated with residual, reducible and carbonate fractions. The Risk Assessment Code reveal that about 30–50% of lead at most of the sites exist in exchangeable fraction while 30–50% of cadmium at almost all the sites is either exchangeable or carbonate bound and therefore comes under the high risk category and can easily enter the food chain. Most of the copper is in immobile fraction at Delhi while at other sites, a sizable portion (10–30%) is found in carbonate fraction thus posing medium risk for the aquatic environment. Fractionation pattern of zinc shows low to medium risk to aquatic environment.

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1. Introduction

During recent years, the pollution of riverine system by heavy metals has attracted a lot of attention of the scientific community. Unlike organic pollutants, natural processes of decomposition do not remove heavy metals. On the contrary, they may be enriched by organisms and can be converted to organic complexes, which may be even more toxic. Metals are introduced into the aquatic system as a result of weathering of soil and rocks, from volcanic eruptions and from a variety of human activities involving mining, processing and use of metals and/or substances containing metal contaminants. Trace metals entering natural water become part of the water-sediment system and their distribution processes are controlled by a dynamic set of physical–chemical interactions and equilibria. The metal solubility is

principally controlled by pH, concentration and type of ligands and chelating agents, oxidation-state of the mineral components and the redox environment of the system. Since each form may have different bioavailability and toxicity, the environmentalists are rightly concerned about the exact forms of metal present in the aquatic environment. The measurement of total metal may not be able to provide information about the exact dimension of pollution and thus the determination of different fractions assumes great importance.

The concept of speciation dates back to 1954 when Goldberg introduced the concept of speciation to improve the understanding of the biogeochemical cycling of trace elements in seawater. Kinetic and thermodynamic information together with the analytical data made it possible to differentiate between oxidized versus reduced, complexed or chelated versus free metal ions in solution and dissolved between particulate species. Florence [1] has defined the term speciation

E-mail address: ckj@nih.ernet.in (C.K. Jain).

analysis as the determination of the individual physico-chemical forms of the element, which together make up its total concentration in a sample. According to Lung [2], speciation analysis involves the use of analytical methods that can provide information about the physico-chemical forms of the elements. Schroeder [3] distinguishes physical speciation, which involves differentiation of the physical size or the physical properties of the metal, and chemical speciation, which entails differentiation among the various chemical forms. The main objective of measuring metal species relates to their relative toxicities to aquatic biota. The second and long-term aim of speciation studies is to advance an understanding of metal interactions between water and bed-sediments in an aquatic ecosystem.

In the last decade researchers have followed different sequential extraction techniques for the fractionation of metals in sediments of different river systems. Rauret et al. [4] studied the speciation of copper and lead in the sediments of River Tenes (Spain) while Pardo et al. [5] studies the speciation of zinc, cadmium, lead, copper nickel and cobalt in the sediments of Pisuerga River, Spain, in order to establish the extent to which these are polluted and their capacity to remobilization. Jardo and Nickless [6] investigated the chemical association of zinc, cadmium, lead and copper in soils and sediments of England and Wales. In most samples, these four metals were associated with all the chemical fractions. Tessier et al. [7] studied speciation of cadmium, cobalt, copper, nickel, lead, zinc, iron and manganese in water and sediments of St. Francois river, Quebec, Canada. Elsokkary and Muller [8] studied speciation of chromium, nickel, lead and cadmium in the sediments of Nile River, Egypt, reporting that a high proportion of chromium, nickel and lead is bound to organic material and sulphides, while cadmium is bound to carbonate fraction. Ure [9] and Rauret [10] have reviewed the chemical extraction procedures used for heavy metal determinations in contaminated soils and sediments. Owing to the need for validation of extraction schemes, the EC Measurement and Testing Programme (formerly BCR) has organized a project for improving the quality of determinations of extractable trace metals, where development and validation of extraction procedures has been discussed [11,12]. Although the importance of metal speciation and fractionation has been realized in developed countries, the subject has not really taken off in our country and only few references are available on the speciation of metals in Indian rivers [13–16].

The River Yamuna is one of the major rivers of the country and traverses a distance of 1376 km from its source in the Himalayas to its confluence with River Ganga at Allahabad. In addition to the traditional and religious bearing associated with the river, the water of the River Yamuna is being used for irrigation, domestic and industrial purposes. During the last few decades

there has been a rapid industrial development in the Yamuna basin. A number of towns and cities in the catchment area have very little or no waste treatment and disposal facilities. Most of the domestic and industrial waste thus gains access into the river. As a result some pockets of the river are believed to be intensely polluted and serve as reservoirs of a variety of organic and inorganic pollutants. Some of the tributaries, which meet River Yamuna at different points also, transfer their pollution load to it.

In spite of the significance of River Yamuna for a large population of the Northern region of India, no systematic study on the metal fractionation in sediments of River Yamuna has been carried out yet. In the light of above facts, it is considered worth while to study the fractionation of heavy metals on the bed sediments of River Yamuna to determine the ecotoxic potential of these metals. By studying the distribution of metals between different phases, their bioavailability and toxicity can be ascertained. The fractions introduced by human activities include the adsorptive and the exchangeable ones and bound to carbonates, which are considered to be weakly bound and may equilibrate with aqueous phase thus becoming more rapidly bioavailable.

2. The river system

The River Yamuna originates from the Yamunotri glacier, 6387m above mean sea level (msl), at the Banderpoonch peak in the Uttarkashi district of Uttaranchal. The catchment of the river extends to states of Uttar Pradesh, Himachal Pradesh, Haryana, Rajasthan and Madhya Pradesh and the entire union territory of Delhi. The river flows 1367 km from here to its confluence with the River Ganga at Allahabad. The main tributaries joining the river include the Hindon, Chambal, Sind, Betwa and Ken (Fig. 1). The annual flow of the river is about 10,000 cumecs. The annual usage is 4400 cumecs, irrigation accounting for 96% of this [17].

On the basis of the different geological and ecological characteristics, the river has been divided into five segments—Himalayan, Upper, Delhi, Eutrophicated and Diluted—of which Delhi is the most polluted stretch of the river. The 172 km long stretch of the river from its source to the Tajewala barrage is called the Himalayan segment. The stretch from Tajewala barrage to the Wazirabad barrage, when the river flows 224 km through Haryana, is the upper segment. The Delhi segment comprises the 22 km that the river traverses in Delhi from Wazirabad barrage to the Okhla barrage. From Okhla barrage to its confluence with the Chambal, 490 km downstream, is the Eutrophicated segment. Beyond this point to its confluence with River Ganga at Allahabad is the Diluted segment (Fig. 2).

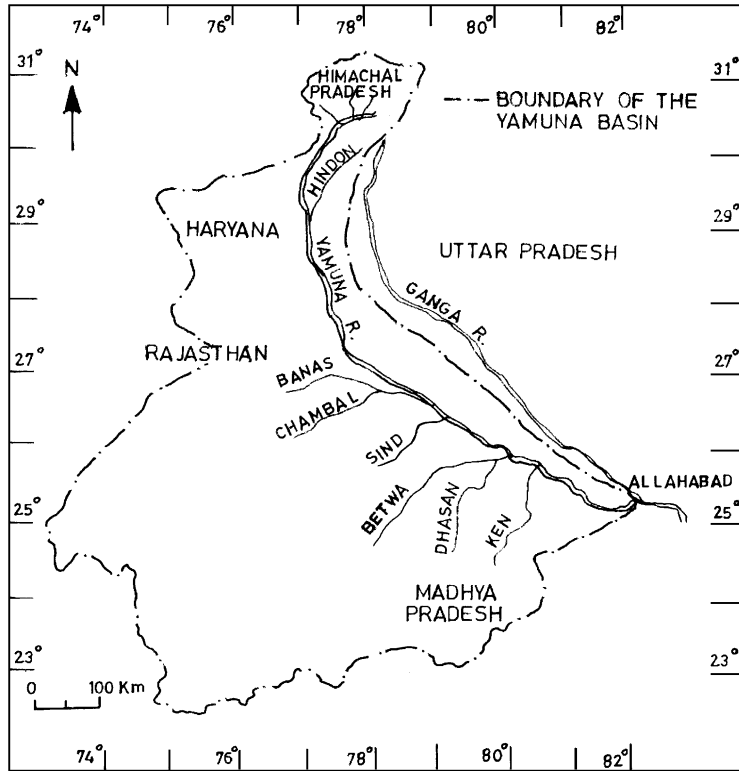


Fig. 1. The Yamuna basin.

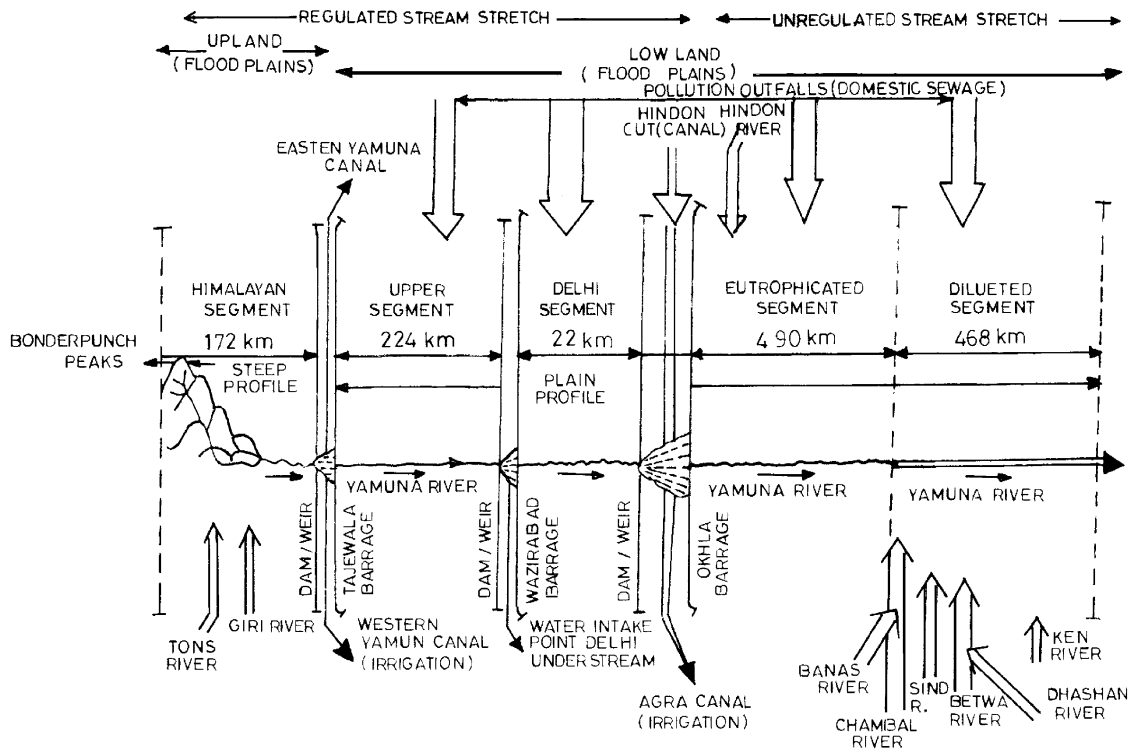


Fig. 2. The five segments of the River Yamuna.

The ground levels in the basin vary from about 6320 m above mean sea level near the Yamnotri glacier to around 100 m above msl at its confluence with River Ganga at Allahabad. The average annual rainfall in the basin is about 1200 mm, the major part of which is received during the monsoon period (June to September). The upper hilly region receives maximum annual rainfall upto 1600 mm while the minimum annual rainfall of about 400 mm occurs in the western parts of the basin. The river receives treated and untreated effluents from various towns and cities located on its banks. The major industrial towns at its banks before their confluence at Allahabad are Yamunanagar, Delhi, Mathura and Agra.

3. Sampling points

The following ten sampling sites on River Yamuna were chosen for the study (Fig. 3).

1. *Wazirabad Barrage*: This is the first site chosen for the study on River Yamuna. The river enters in Delhi at this site and an important intake water works for the city's water supply is located here.
2. *Okhla Barrage*: Through Barapulla drain, a part of the city's waste gets dumped into the River Yamuna at this site. This one is also characterized by the confluence of River Hindon, which drains some of the industrial towns of western Uttar Pradesh. This station also gives an idea of the cumulative effect of pollution of the River Yamuna in its flow in the Delhi area.
3. *Palwal*: The site gives an idea of the cumulative effect of pollution in its flow through Faridabad and Ballabgarh.
4. *Mathura*: The site is downstream of all bathing ghats and the Masani drain. The drain brings wastes from textile printing industrial complex. The discharge from the Mathura refinery meets River Yamuna after this site.

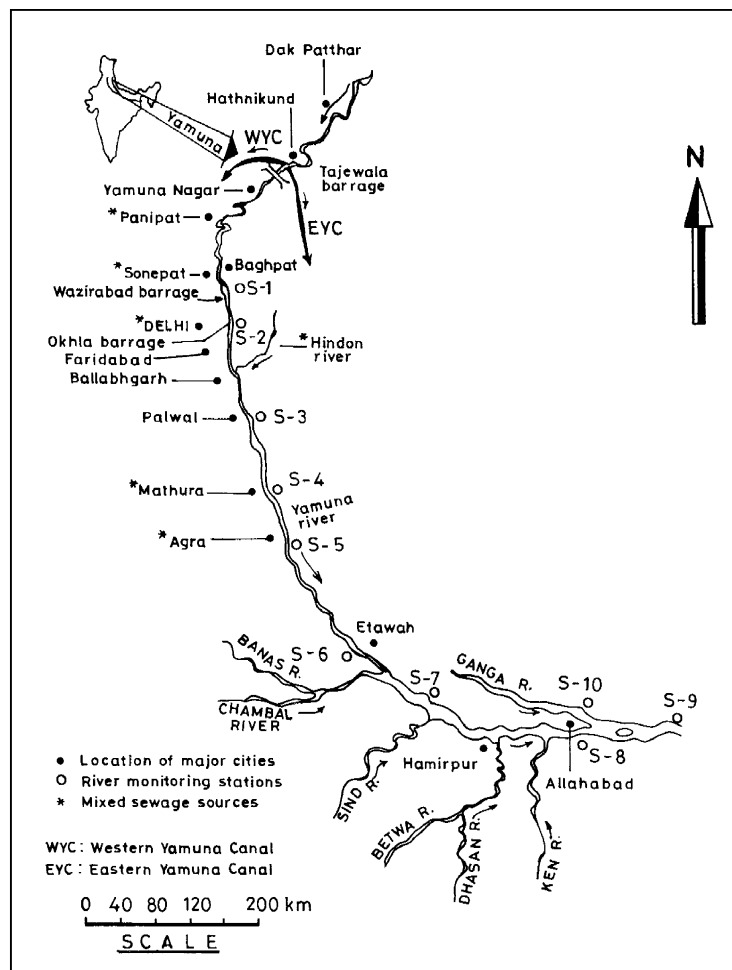


Fig. 3. The Yamuna River showing location of major cities and sampling sites

5. *Agra*: The site is located on River Yamuna downstream of the city of Agra behind Taj Mahal. The different drains of the city meet the river before this point and the city's water supply is drawn from the river a few kilometers upstream of this site.
6. *Etawa*: The site is located before the confluence of River Chambal at Etawa.
7. *Kalpi*: The site is located after the confluence of River Sind at Kalpi.
8. *Allahabad*: The site is located before the confluence of River Yamuna with River Ganga.
9. *Confluence of Ganga and Yamuna at Allahabad*: This site is located after the confluence of River Yamuna with River Ganga at Sangam. This station gives an idea of the cumulative effect of pollution of River Yamuna and Ganga at Allahabad.
10. *Ganga at Allahabad*: This site is located at River Ganga at Sangam before its confluence with River Yamuna.

4. Methodology

Freshly deposited sediments from shallow water near the banks of River Yamuna at different sites were collected in polyethylene bags and brought to the laboratory. The samples were collected with the help of plastic scoop during the dry period in the months of May and June 2001. The samples were taken from the upper 5 cm of the sediments at places where flow rates were low and sedimentation was assumed to occur [18,19], air dried and stored in refrigerator for further analysis.

pH: 10 g of the air dried sample was taken in 50 ml distilled water and agitated for 5 min. The solution was left undisturbed for 1 h with occasional shaking before measuring the pH.

Carbonate content: 5.0 g of sediment sample was treated with 1.0 N HCl and the unused acid was titrated with 1.0 N NaOH.

Organic matter: Organic matter in the sediment was determined by wet oxidation–redox titration method using an acid dichromate solution. The reported data are the sum of soluble and insoluble organic carbon.

Metal extraction: The total metals were extracted from the sediment samples using an acid digestion mixture (HF + HClO₄ + HNO₃) in an open system. The 0.5 g of sediment sample was treated with 10 ml HF and 2 ml HClO₄ and heated on hot plate upto dryness. The residue was further treated first with 5 ml perchloric acid and then with 5 ml HNO₃ and heated upto dryness. The residue was finally dissolved in 1:1 HCl.

4.1. Metal fractionation

The air dried sediment samples were sieved to obtain 75 μm sediment fraction. The sequential extraction

technique proposed by Tessier et al. [20] was followed for partitioning the trace metals into the following five fractions:

1. *Exchangeable*: 1.0 g sediment sample was extracted at room temperature for 1 h with 10 ml of 1.0 M MgCl₂ (pH 7.0) with continuous agitation.
2. *Bound to carbonates*: The residue obtained from step (1) was leached at room temperature with 10 ml of 1.0 M sodium acetate adjusted to pH 5.0 with acetic acid. The mixture was agitated for 5 h.
3. *Bound to Fe–Mn oxides*: The residue obtained from step (2) was refluxed at 100°C with 20 ml of 0.04 M NH₂OH. HCl in 25% (v/v) acetic acid for 6 h.
4. *Bound to organic matter*: To the residue obtained from step (3), 3 ml of 0.02 M HNO₃ and 5 ml of 30% H₂O₂ were added and pH adjusted to 2.0 with HNO₃. The mixture was refluxed at 100°C for 2 h. A second 3 ml aliquot of 30% H₂O₂ (pH 2 with HNO₃) was then added and the sample was again refluxed for 3 h. After cooling, 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO₃ was added. The sample was diluted to 100 ml and agitated continuously for 30 min. The addition of ammonium acetate is designed to prevent adsorption of extracted metals onto the oxidized sediment.
5. *Residual*: The residue obtained from step (4) was digested with a HF–HClO₄ mixture as per procedure followed for the analysis of trace elements.

4.2. Metal ion analysis

Metal ion concentrations in different extracts were determined by flame atomic absorption spectrometry using Perkin-Elmer atomic absorption spectrometer (Model 3110) using air-acetylene flame. Operational conditions were adjusted in accordance with the manufacturer's guidelines to yield optimal determination. Quantification of metals was based upon calibration curves of standard solutions of respective metals. These calibration curves were determined several times during the period of analysis. The detection limits for various metal ions are 0.001, 0.01, 0.0005 and 0.0008 mg/l for copper, lead, cadmium and zinc, respectively.

5. Results and discussion

The sediment under study has a rather coarse texture. The pH and organic content at different sites of River Yamuna are given in Table 1. The pH of the sediment varies from 8.01 to 8.45 indicating alkaline nature of the sediments. The organic content of the sediment was of the order of 1–2% at most of the sites except S-2 and S-3 where organic content was found to be 7.87% and

5.94%, respectively. The high values of organic content at sites S-2 and S-3 is due to discharge of huge amount of sewage and industrial wastes from municipal and industrial areas of Delhi. It is worth mentioning here

that Delhi is the largest contributor of pollution to the river receiving almost 80% of pollution load through various drains between Wazirabad and Okhla.

5.1. Metal enrichment

The longitudinal variation of different metals is shown in Fig. 4. The total copper shows higher concentrations at site S-2 and S-3 and then remains more or less constant along the river with the exception of site S-10. The total lead also shows similar trends with highest value at site S-1 and S-3 and then slightly decreasing trend upto site S-6. After this total lead content again shows an increasing trend. The total cadmium load does not show any significant spatial variation. However, its concentration is quite higher as compared to the other rivers of the world [18,21,22]. Higher pH observed in the sediments may be partly contributing to the increased concentration of cadmium

Table 1
Characteristics of sediment

Site	pH	Organic matter (%)
S-1	8.45	1.46
S-2	8.13	6.87
S-3	8.00	5.94
S-4	8.13	1.36
S-5	8.02	1.21
S-6	8.31	1.23
S-7	8.01	1.16
S-8	8.23	1.04
S-9	8.21	1.25
S-10	8.16	1.09

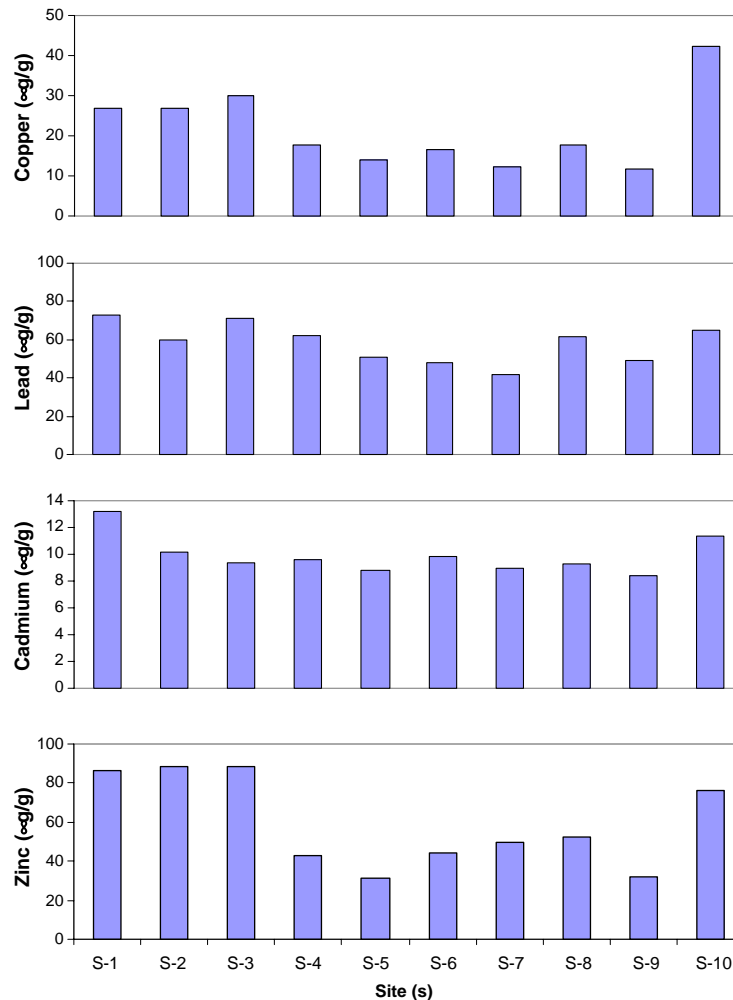


Fig. 4. Longitudinal variation of total metal concentrations in bed sediments.

in the sediments due to precipitation of dissolved cadmium. The total zinc also shows higher values at site S-2 and S-3 and then quite lower values along the river.

A comparison of metal concentration in the sediments with the shale standard is generally taken as a quick and practical method of tracing heavy metal enrichment. The average shale values along with the metal concentrations reported by other workers on some of the important rivers of the world [18,19,21–24] have been summarized in Table 2.

The average metal concentration in the sediments of River Yamuna reveals that the concentration of copper and zinc is lower whereas that of lead and cadmium are higher than the respective average shale values. Sitasward [24] has reported higher concentrations of copper, and zinc in the bed sediments of the River Yamuna as compared to the results of present study whereas the lead concentration is almost same. The difference may be attributed to the fact that the study carried out by Sitasward [24] is confined only to Delhi area while in the present investigations the sampling sites cover a much longer stretch to assess the pollutional load due to anthropogenic inputs. A comparison of the present study results with the other rivers reveals that the average metal load of lead and cadmium is quite higher in the sediments of the River Yamuna.

Another method of indicating the metal enrichment in the sediments is the comparison of the metal concentration ratios. In the natural river systems, elements as well as metals exist together in relative proportions to each other. These ratios are dependent on a large number of processes in a geochemical cycle including weathering, transport and deposition. Ratios of trace metals to conservative elements may reveal the geochemical imbalances due to elevated trace metal concentrations normally attributed to anthropogenic activities.

Table 3 shows the trace metal to iron ratios at different sampling sites of the River Yamuna. The metal pair ratios clearly reflect maximum enrichment of copper at site S-2 followed by S-3 and S-1; lead shows maximum enrichment at site S-2 followed by S-1 and S-5; cadmium shows enrichment at site S-5 and zinc shows enrichment at site S-1, S-2 and S-3.

5.2. Fractionation studies

The major mechanism of accumulation of heavy metals in sediments lead to the existence of five categories, viz., exchangeable, bound to carbonate, bound to reducible phases (iron and manganese), bound to organic matter and residual. These categories have different behaviour with respect to remobilization under changing environmental conditions. There are two basic

Table 2
Concentration of heavy metals in sediments of different rivers of the world and average shale values ($\mu\text{g/g}$)

River	Cu	Pb	Cd	Zn	Reference
Ganga	10.8	25.6	2.55	36.1	[22]
Ganga	21.0	25.0	—	46.0	[19]
Brahmaputra	17.0	—	—	47.0	[19]
Genesse, USA	18.0	40.0	—	69.0	[23]
Toyohira, Japan	22.0	24.0	0.20	152.0	[18]
Illinois, USA	19.0	28.0	2.0	81.0	[21]
Average shale	45.0	20.0	0.3	95.0	[25]
Yamuna	52.0	57.0	—	123.0	[24]
Yamuna (Present study)	22.2	60.3	9.5	59.2	—

Table 3
Metal pair ratio (M/Fe) for heavy metal content in bed sediments

Sites	Cu ($\times 10^{-3}$)	Pb ($\times 10^{-3}$)	Cd ($\times 10^{-3}$)	Zn ($\times 10^{-3}$)
S-1	1.53	4.16	0.52	4.93
S-2	1.92	4.38	0.56	4.86
S-3	1.63	3.88	0.51	4.81
S-4	0.64	2.24	0.35	1.55
S-5	1.11	4.05	0.70	2.49
S-6	0.68	1.97	0.40	1.81
S-7	0.98	1.51	0.26	1.78
S-8	0.94	3.17	0.68	3.74
S-9	0.92	3.90	0.66	2.51
S-10	0.76	2.61	0.39	2.24

approaches for fractionation in sediments. The theoretical one based upon thermodynamic calculations suffers from incomplete data. The experimental determination implies a separation of the above said five different fractions by using a sequential extraction procedure.

The methods of fractionation of trace metals in sediments are based on sequential extraction procedures. In the present study, sequential extraction procedure as proposed by Tessier et al. [20] has been used to obtain the following five fractions: (1) exchangeable; (2) bound to carbonate phases; (3) bound to reducible phases (iron and manganese oxides); (4) bound to organic matter and sulfides; and (5) residual.

By studying the distribution of the metals between the different phases, their bioavailability and toxicity can be ascertained. The fractions introduced by man's activity include the adsorptive and exchangeable and bound to carbonates which are considered to be weakly bound and may equilibrate with aqueous phase thus becoming more rapidly bioavailable [26]. The metal present in the inert fraction, being of detrital and lattice origin, can be taken as a measure of contribution by natural sources [27]. The Fe–Mn oxide and the organic matter have a scavenging effect and may provide a sink for heavy metals. The release of the metals from this matrix will most likely to be affected by the redox potential and pH. The speciation pattern of different metals in the bed sediments of River Yamuna at different sites are given in Fig. 5.

Fractionation profile of copper shows that a major portion is bound to residual fraction at site S-1 while at site S-2 and S-3 maximum portion is bound to organic matter probably due to its more pronounced tendency for complexation with organic matter at these sites. A high percentage of copper is also found in reducible fraction (Fe–Mn oxide) and residual fraction and much lower contents are associated with exchangeable and carbonate fractions at site S-2 and S-3. At other sites, copper is mainly associated with residual, reducible and carbonate fractions. Gibbs [26] reported higher percentage of copper in the residual fraction and the concentration of copper bound to Fe–Mn oxides and organic matter was much lower. The present investigations suggest that copper has a tendency to remain associated with residual, reducible and carbonate fractions.

The fractionation profile of lead suggests that at site S-1 major portion of lead is associated with residual fraction and moderate contribution is being made by exchangeable fraction while at site S-2 major portion is associated with Fe–Mn oxide fraction and moderate contribution being made by residual and exchangeable fraction. At other sites, major portion of lead is associated with exchangeable and residual fraction and contents of these two fraction increase along the river down stream. Jha et al. [15] also reported that lead is

mostly present in Fe–Mn oxide fraction in sediments of River Yamuna at Delhi.

The fractionation profile for cadmium indicates that it is mostly bound to exchangeable, carbonate and residual fractions, the rest being present in Fe–Mn oxide fraction and reducible fraction. No significant spatial variation was observed in the speciation pattern of cadmium in the bed sediments of River Yamuna. Tessier et al. [7] reported that a large amount of cadmium was found in the exchangeable and carbonates fractions in Yamaska and St. Francois River sediments. The major fraction of cadmium in carbonate form would imply that an appreciable percentage of cadmium would have been remobilized becoming readily available following a slight lowering of pH.

The fractionation profile of zinc indicates that major portion of zinc is associated with residual fraction. There are also appropriate concentrations associated with carbonate and reducible phases. The above results are in accordance with those reported by Jardo and Nickless [6], Pardo et al. [5] and Tessier et al. [7].

It is evident from the results of the fractionation studies that the metals in the sediments are bound to different fractions with different strengths. The strength values can, therefore, give a clear indication of sediment reactivity, which in turn assess the risk connected with the presence of metals in an aquatic environment. This criteria (risk assessment code (RAC)) as given below indicates that a sediment which can release in exchangeable and carbonate fractions, less than 1% of the total metal will be considered safe for the environment. On the contrary, a sediment releasing in the same fraction more than 50% of the total metal has to be considered highly dangerous and can easily enter the food chain [28].

Risk assessment code (RAC)	Criteria (%)
No risk	<1
Low risk	1–10
Medium risk	11–30
High risk	31–50
Very high risk	> 50

The code as applied to the present study reveals that about 30–50% of lead at most of the sites exist in exchangeable fraction while 30–50% of cadmium at almost all the sites is either exchangeable or carbonate bound and therefore comes under the high risk category and can easily enter the food chain. Because of the toxicity and availability of cadmium, it can pose serious problems to the ecosystem. The total lead in the sediments is quite high and its association with exchangeable fraction may cause deleterious effects. Most of the copper is in immobile fraction at site

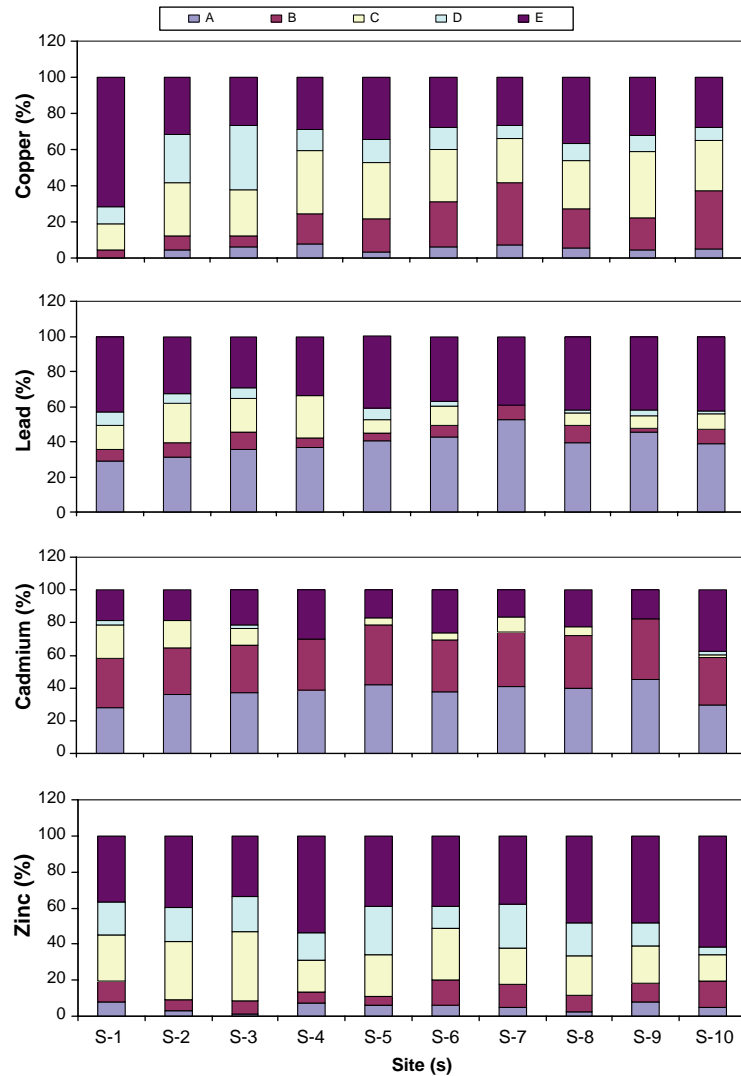


Fig. 5. Fractionation of different metals in bed sediments.

S-1 and S-2 while at other sites a sizable portion (10–30%) is found in carbonate fraction thus posing medium risk for the aquatic environment. Speciation pattern of Zinc shows low to medium risk to aquatic environment. Zinc besides having less environmental risk is present in forms from which it cannot be easily leached out.

6. Conclusion

The fractionation approach presented in the paper open a new dimension in the area of river water quality monitoring to determine the ecotoxic potential of metal ions. The sediments of the River Yamuna have a rather

coarse texture and are alkaline in nature. There is considerable enrichment of metals at Delhi. Amongst the different metals studied cadmium concentration was the lowest but a major portion of it (30–50%) is contained in the most mobile fraction (either exchangeable or carbonate bound) and therefore can easily enter the food chain. About 30–50% of the lead at most of the sites exist in exchangeable fraction and thus exert a potential hazard for the aquatic environment. Most copper is in immobile fraction at Delhi while at other sites a sizable portion (10–30%) is found in carbonate fraction thus posing medium risk for the aquatic environment. Speciation pattern of zinc shows only low to medium risk for the aquatic environment.

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