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Environmental mobility and geochemical partitioning of Fe, Mn, Co, Ni and Mo in sediments of an urban river

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Environmental mobility and geochemical partitioning of iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni) and molybdenum (Mo) were examined in sediments collected from the whole old Nakagawa river (NR), Tokyo, Japan. A combined 6- step sequential extraction procedure was employed for the partitioning of the metals and the concentrations were measured in the liquid extracts by atomic absorption spectrophotometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS). The observed order of potential mobility of metals in the aquatic system of NR was: Ni > Co > Mo > Mn > Fe. The association of Co, Ni and Mo (26.6-30.5; 23.2-38.5 and 19.0-40.1% of total, respectively) were found highest with amorphous Fe oxyhydroxide phase, and the maximum fraction of Fe and Mn were in silicates and residual phase. The normalization of the concentrations of metals using Al as a conservative element confirmed that most of the sampling stations of NR were enriched with Ni, Mo and Mn. Geoaccumulation index (I_{geo}) values for most of the sites have higher for Ni and Mo. Environmental risk of metals were also evaluated by using risk assessment code (RAC) and found medium risk for Ni, Mo, Co and Mn.

Key words: Mobility, partitioning, pollution, metals, sediment.

INTRODUCTION

Urbanization is of considerable importance for socio-economic growth and is continuously modifying the physical, chemical and biological composition of our living environment. As a result, millions of people living in and around urban centres are exposed to an unnatural and unhealthy environment. Sediments are important carriers of metals in the environment and reflect the current

quality of the system. As in natural environments, urban river sediments have a high potential for storage of different metals. Unlike natural rivers, however, a large proportion of the element load contained in urban sediments is not associated with the original geologic parent material, but with the steady supply of those elements, both dissolved and in particulate form. Thus, a river close to an urban centre has the opportunity to be polluted by both naturally occurring and anthropogenically originated metals. Undoubtedly, natural sources come from physical and chemical weathering of parent materials (rocks and minerals) of the river area and the anthropogenic sources include industrialization, wastes and sewage effluents from urban centres, underground deposition of industrial wastes and others.

The banks of NR in Tokyo, Japan is a location where a significant amount of different types of industrial units were available at the time of second world war (USAMS,

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Abbreviations: Fe, Iron; Mn, manganese; Co, cobalt; Ni, nickel; Mo, molybdenum; NR, Nakagawa river; AAS, atomic absorption spectrophotometry; ICP-MS, inductively coupled plasma mass spectrometry; RAC, risk assessment code; ICP-MS, inductively coupled plasma- mass spectrometry; AR, Arakawa river; OR, Onaki river.

1945-46) and a huge amount of industrial metal (mainly Cr) contained waste was deposited about 30 years ago (Zakir, 2008; Zakir et al., 2008).

Metals are usually distributed throughout the sediment components and associated with them in various geochemical forms including ion exchange, adsorption, precipitation, and complexation. Due to changes in environmental conditions, such as acidification, appearance of strong current, dredgings, redox potential or organic ligand concentrations, oxidation state and others can cause mobilization of metals from solid to liquid phase. Then metals accumulated in sediments can cause contamination of surrounding waters and represent a potential risk for an aquatic environment. Heavy metals are most important among the frequently observed contaminants in the environment. Both industrial activities and urbanization have greatly increased the metal burden in the environment. In Japan, there has been variable human damage caused by heavy metals, such as Cu poisoning in the Ashio Cu mine area and the Itai-itai disease induced by Cd in the Kamioka mine area.

In sediments, metals can be present in a number of chemical forms, and generally exhibit different physical and chemical behaviour in terms of chemical interaction, mobility, biological availability and potential toxicity, which has been demonstrated by several authors (Amiard et al., 2007; Zakir et al., 2008; Wang et al., 2010). Therefore, it is necessary to identify and quantify the forms in which a metal is present in sediment to gain a more precise understanding of the potential and actual impacts of elevated levels of metals in sediments and to evaluate processes of downstream transport, deposition and release under changing environmental conditions. Methods for the determination of different forms of metals in sediments include sequential extraction, whereby a series of reagents is used to extract operationally defined discrete phases from sediments in an outlined sequence. The overall behaviour of metals in an aquatic environment is strongly influenced by the associations of metals with various geochemical phases in sediments (Horowitz, 1991).

Sequential extraction techniques have been applied to study the geochemical partitioning of metals in contaminated soils (Hickey and Kittrick, 1984; Basta and Gradwohl, 2000) and sediments (Pardo et al., 1990; Jain, 2004; Morillo et al., 2004; Zakir and Shikazono, 2008). Geochemical distribution results have also been used as an aid in predicting potential contaminant mobility and bioavailability (Pueyo et al., 2003; Zakir et al., 2008). This could help us to understand the geochemical processes governing metal mobilization and potential risks induced. According to Singh et al. (2005), there are five major mechanisms of accumulation of metals in sediment, namely- exchangeable, bound to carbonate, bound to reducible phases (amorphous Fe oxyhydroxide and crystalline Fe-oxide), bound to organic matter (oxidizable fraction) and residual. These categories have different

behaviours with respect to remobilization under changing environmental conditions. The fractions introduced by anthropogenic activity include the adsorptive, exchangeable and bound to carbonate fractions. These are considered to be weakly bounded metals, which may equilibrate with the aqueous phase and thus become more rapidly bioavailable (Pardo et al., 1990).

In this study, sediment samples from a river in an urbanized area of Japan were analyzed by sequential extraction scheme to measure the geochemical distribution of Fe, Mn, Co, Ni and Mo; to assess the environmental mobility of aforementioned metals and to determine the pollution levels in sediments due to different anthropogenic activities.

MATERIALS AND METHODS

General description of the study area

NR is located in the eastern part of Tokyo (Edogawa ward) with a length of about 5 km. Both side of the river is connected with Arakawa river (AR) by sluice gates and with Onaki river (OR) by a narrow channel. Depth, width, flow of current and water level (about 3 m) in AR is higher than the NR and OR. There were several types of small and large industrial units on both banks of NR during 40th century (USAMA, 1945-46), such as refinery and mineral oil company, several chemical and steel company, paper and pulp mills, soap industry, hide and tanning factory, paints and dyeing industry and others, and still the river is received a significant amount of various industrial waste and house hold discharge from residential areas (Zakir, 2008).

The area mainly consists of tertiary and quaternary sedimentary rocks (shale and sandstone) overlain by quaternary volcanic materials and weathered soils of volcanic origin. Alluvium sediments consisting of various kinds of rock fragments (granite, basalt, chert, limestone, shale, sandstone) were derived from upper stream region where Paleozoic rocks are distributed (Omori et al., 1986). Among the clay minerals, vermiculite was dominant, and chlorite and illite were also observed. These crystalline clay minerals were deduced to be derived from aeolian mica that was contained in a coast deposit distributed along coasts of this region, and might be mixed with volcanic ash soils (Takesako et al., 2002).

Collection and preparation of samples

A total of 21 sediment samples were collected, among those 17 were from NR, 2 from OR and the other 2 from AR, as described in Figure 1. The sampling distance from one station to another was at least about 100 m. The surface sediment samples were taken from 0-10 cm and quickly packed in airtight polythene bags. The sample mass collected in each case was about 500 g. Sub-samples of the material were oven dried at 50°C for 24 h and sieved (aperture 125 µm). The lower particle size fraction was homogenized by grinding in an agate mortar and stored in glass bottles for chemical analyses.

Reagents

All chemicals and reagents were of analytical reagent grade quality (Sigma-Aldrich, USA and Wako, Japan). Millipore water (18 MΩ) was used throughout all the experiments. Before use, all glass and plastic ware were soaked in 14% HNO₃ for 24 h. The washing was

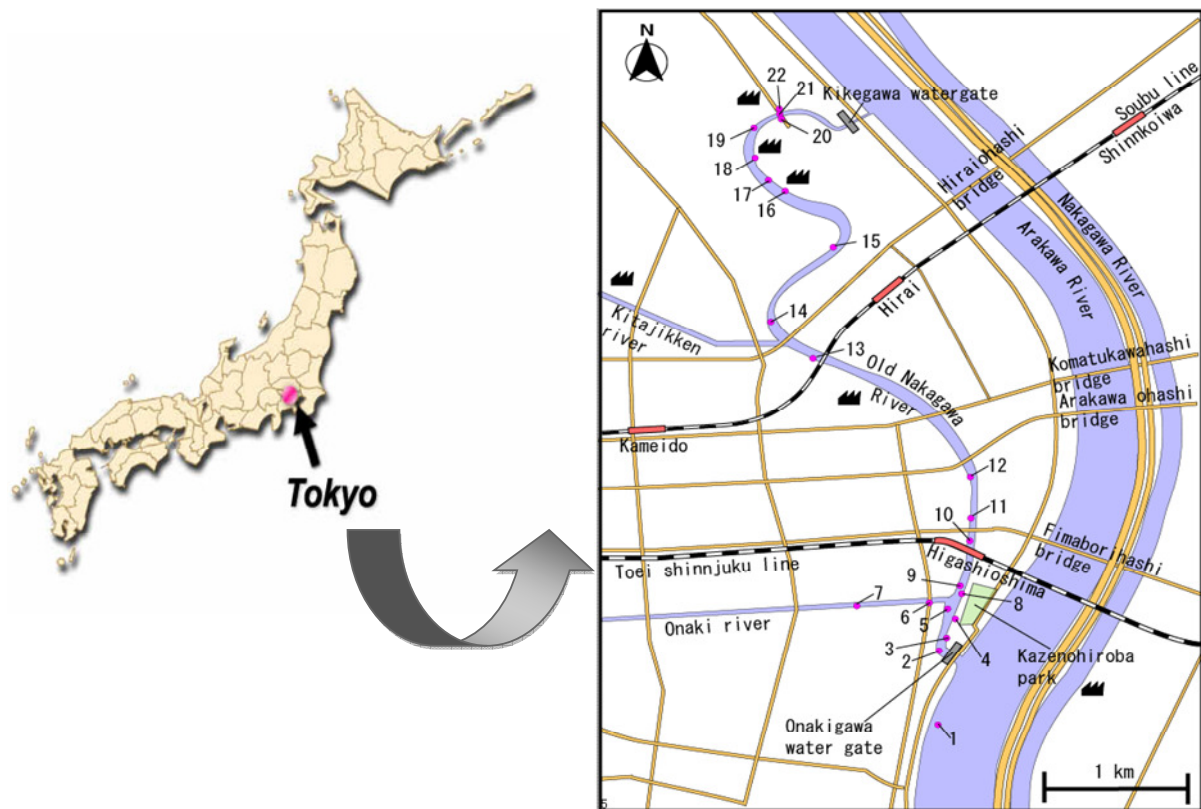


Figure 1. Locations of the sampling stations in Old Nakagawa, Onaki and Arakawa rivers.

completed with Millipore water rinse.

Apparatus and instrumentations

Atomic absorption measurements for Fe and Mn were performed with a Hitachi Z-6100 polarized Zeeman spectrophotometer, equipped with single element hollow-cathode lamps. The instrument was operated at maximum sensitivity with an air-acetylene flame.

Lamp intensity and band pass were used according to the manufacturer's recommendations. A centrifuge (Kokusan H-27F, Tokyo, Japan) for complete separation of

the extract from the residue, a Yamato SA-320 (Tokyo, Japan) shaker and a TOA-DKK HM-20P (Tokyo, Japan) pH meter were used throughout all the experiments. Inductively coupled plasma-mass spectrometry (ICP-MS, Hewlett-Packard 4500, USA) was applied for determination of Co, Mo and Ni in this study. A Bruker AXS: D-8 Advance (Berlin, Germany) X-ray diffractometer was employed for XRD analysis.

Sequential extraction experiment

The sequential extraction scheme adopted in this study

was a combination of Tessier et al. (1979) and Hall et al. (1996) schemes. The first two (2) steps were adopted from the procedure proposed by Tessier et al. (1979), which will provide more information about the availability of the metals studied. On the other hand, Zakir et al. (2008) reported that the oxide phase of the sediments of old Nakagawa river is dominant for most of the trace metals, and Hall et al. (1996) scheme has the opportunity to get much more knowledge about the oxide phase as amorphous Fe oxyhydroxide and crystalline Fe oxide. Due to these reasons, the last four (4) steps were adopted from the scheme proposed by Hall et al. (1996). However, the successive chemical extraction steps involved

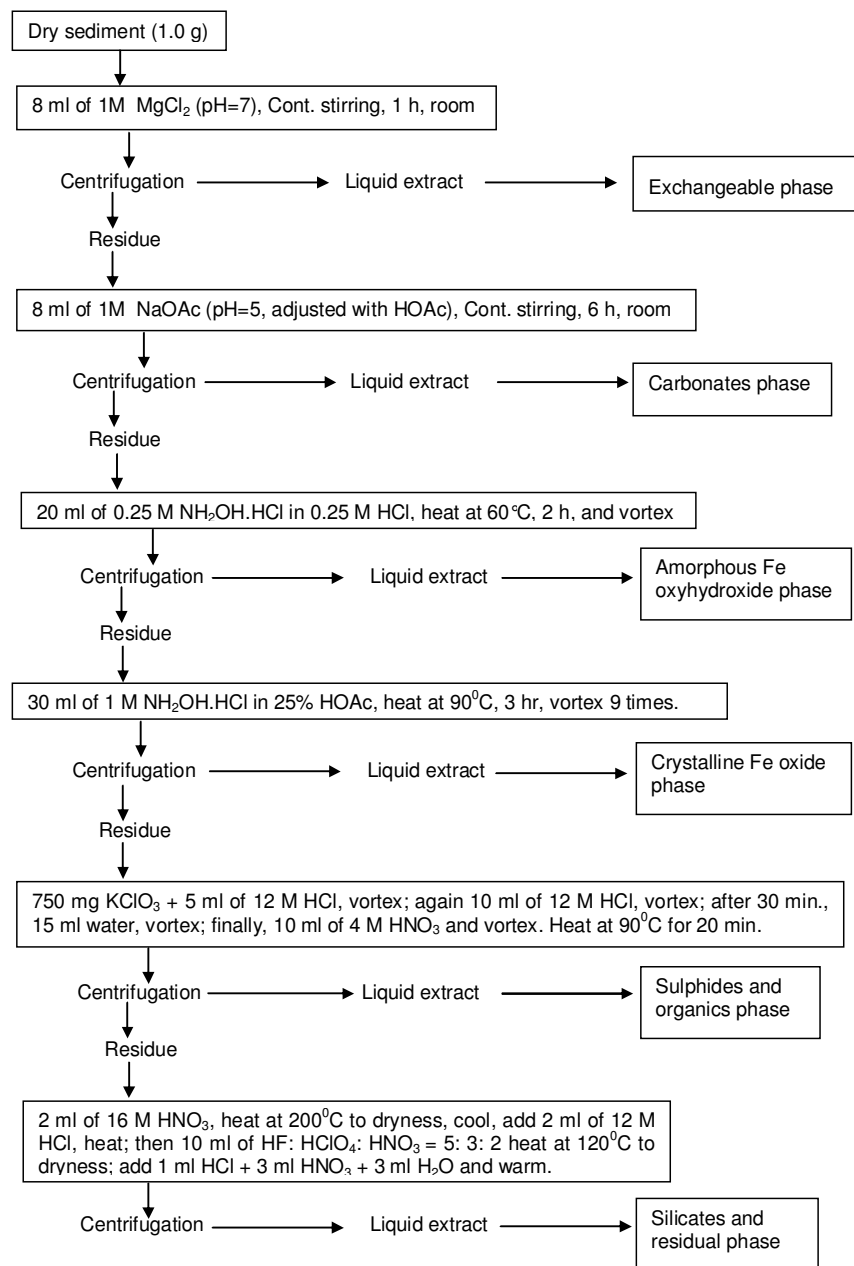


Figure 2. Flow-chart of the sequential extraction scheme used in this study.

in the sequential procedure employed are summarized in the flow-chart presented in Figure 2.

All the operations were carried out in 50 ml polypropylene centrifuge tubes (Nalgene, New York) and Teflon (PTFE) containers provided with screw stoppers. The initial mass of sediment was 1.0 ± 0.0001 g. The extracts were separated from the solid residue by centrifugation at 3000 rpm for 30 min. After each step, the solution was filtered by suction through a $0.45 \mu\text{m}$ Millipore filter, and the filtrate collected in a polyester container. Then the solutions for each step were prepared accordingly for ICP-MS measurement following the manufacturer's recommendations. During extraction, extractant quality (especially the required pH) maintained carefully. A certified reference stream sediment JSd-2, provided by the

geological survey of Japan was also analyzed using the same procedure as check for total concentration and reached 89-107% recovery for the studied metals. As a quality assurance measure, each sediment sample was subjected to triplicate analyses and the measurements are given as mean, unless noted.

Sediment quality assessment

Normalization of metals

In order to account for geochemical variations along the NR of Tokyo, Japan, normalization by a conservative element Al was

Table 1. Classification of risk assessment code (RAC).

RAC	The sum of exchangeable and carbonate bound fractions (in % of total)
No risk	< 1
Low risk	1 - 10
Medium risk	11 - 30
High risk	31 - 50
Very high risk	> 50

used, as geochemical normalization can compensate for both the granulometric and mineralogical variability of metal concentration in sediments (Liu et al., 2003). Consequently, in order to assess the possible anthropogenic impact, several authors (Datta and Subramanian, 1998; Badr et al., 2009; Milacic et al., 2010) have successfully used Al to normalize the metal contaminants. In this study, we have also used Al as a conservative tracer to differentiate natural from anthropogenic components and Earth's crust average (Huheey, 1983) data have been considered as baseline values, as Al is abundant in the earth's crust and is scarcely influenced by anthropogenic inputs.

Determination of geoaccumulation index (I_{geo})

The geoaccumulation index (I_{geo}) values were calculated for Ni, Mo, Co, Mn and Fe as introduced by Muller (1969) is as follows:

$$I_{geo} = \log_2 (C_n / 1.5 \times B_n)$$

Where C_n is the measured concentration of metal in the sediment, and B_n is the geochemical background for the same element which is either directly measured in precivilization sediments of the area or taken from the literature (average shale value described by Turekian and Wedepohl, 1961). The factor 1.5 is introduced to include possible variations of the background values that are due to lithologic variations.

According to Muller (1969), there are seven grades or classes of the geoaccumulation index. Class 0 (practically uncontaminated/unpolluted): $I_{geo} < 0$; Class 1 (Uncontaminated to moderately contaminated): $0 < I_{geo} < 1$; Class 2 (moderately contaminated): $1 < I_{geo} < 2$; Class 3 (moderately to strongly contaminated): $2 < I_{geo} < 3$; Class 4 (strongly contaminated): $3 < I_{geo} < 4$; Class 5 (strongly to extremely contaminated): $4 < I_{geo} < 5$; Class 6 (extremely contaminated): $I_{geo} > 5$, which is an open class and comprises all values of the index higher than Class 5.

Risk assessment code (RAC)

The metals in the sediments are bound with different strengths to the different fractions. The risk assessment code (RAC) as proposed by Perin et al. (1985), mainly applies to the sum of exchangeable and carbonate bound fractions for assessing the availability of metals in sediments (Table 1). If a sediment sample can release in these fractions less than 1% of the total metal will be considered safe for the environment. On the contrary, sediment releasing in the same fractions more than 50% of the total metal has to be considered highly dangerous and can easily enter into the food chain.

RESULTS AND DISCUSSION

Geochemical fractionation profile of Fe, Mn, Co, Ni and Mo

The following sections describe geochemical distribution of Fe, Mn, Co, Ni and Mo according to the sequential extraction procedure applied in this study.

Exchangeable fraction

The fraction of exchangeable metals included the portion, which is held by the electrostatic adsorption as well as those specially adsorbed. The amount of metals in this phase indicated the environmental conditions of the overlying water bodies. Metals in this fraction are the most mobile and readily available for biological uptake in the environment (Singh et al., 2005; Zakir et al., 2008). The exchangeable fraction recovered for Co and Fe in sediments of the study area were comparatively low (0 and 0- 0.98% of total, respectively). On the other hand, the range of Ni, Mo and Mn for this fraction varied from 0-10.3 (0 - 4.1% of total), 0 - 1.0 (0- 7% of total) and 0-108.1 (0- 8% of total) $\mu\text{g g}^{-1}$, respectively in sediments of the study area (Figure 3). The adsorbed/ exchangeable/ carbonate (AEC) fractions recovered for Fe, Mn and Ni in sediments of Nomi river, Tokyo, Japan were also reported low (0.57 - 1.57, 0.66 - 4.11 and 0.60 - 20.06% of total, respectively) (Sharmin et al., 2010). Metals accumulated in this fraction can return to waters in the suspended or dissolved form and represent a potential risk for an aquatic ecology as well as the environment. However, the affinity order of different metals for exchangeable fraction was Ni > Mo > Mn > Fe > Co.

Fraction bound to carbonate

Preferential association of carbonate bound Ni, Co and Mo (on an average 22.1, 18.1 and 16.5% of total, respectively) were found in sediments of the study area (Figure 3), which may readily available following a slight lowering of pH (Jain, 2004; Zakir et al., 2008). Metal recovered by the use of 1 M NaOAc adjusted to pH 5 is associated with carbonate minerals likely to be bioavailable. The XRD data of our previous study also indicate presence of higher amount of carbonate and several clay minerals in sediments of NR (Zakir et al., 2008), which support these findings. However, metals associated with this fraction are not strongly bound to the sediment solids and can be released to the sediment pore water in acidic conditions (pH < 5). Metals in this fraction are adsorbed on sediments or on their essential components namely clays, Fe and Mn, hydroxides or oxyhydroxides and humic acids. Turner and Olsen (2000) determined extractability of metals in contaminated

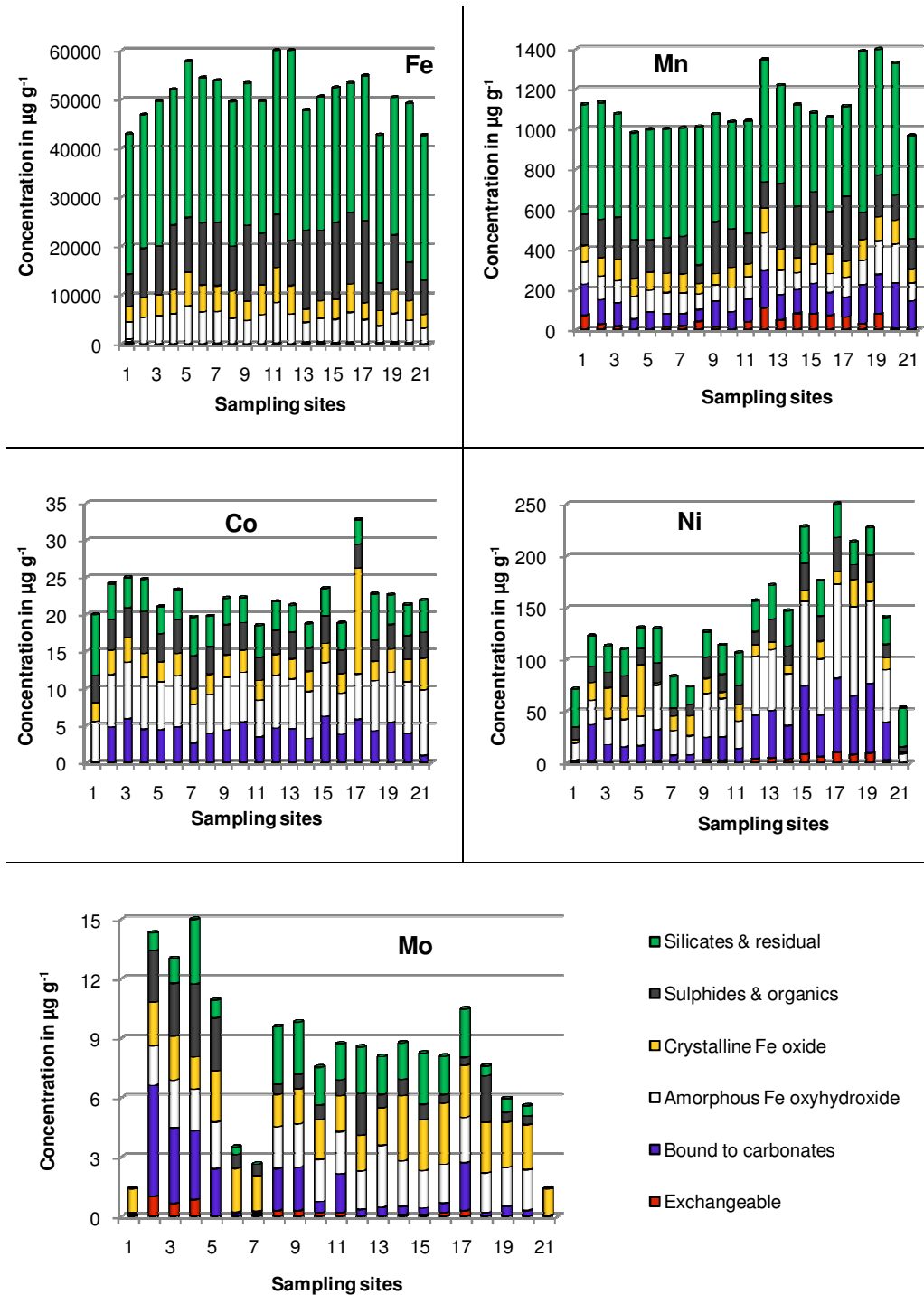


Figure 3. Geochemical distribution of Fe, Mn, Co, Ni and Mo concentration ($\mu\text{g g}^{-1}$) in sediment samples at different sampling sites of the study area.

estuarine sediments by chemical and enzymatic reactions. Among the chemical reagents, acetic acid best represented the fraction that was likely to be bioavailable to sediment ingesting and benthic organisms. Finally association of metals with this fraction is probably the

best example of human-induced influence in the sediments of the study area. On the other hand, fraction bound to carbonate recovered for Fe and Mn in sediments of the study area were comparatively low (on an average 0.14 and 11.1% of total, respectively),

suggesting lower pollution risk (Figure 3). However, the affinity order of different metals for the fraction bound to carbonate was: Ni > Co > Mo > Mn > Fe.

Amorphous Fe oxyhydroxide fraction

Due to the large surface area and surface site, amorphous Fe oxyhydroxide are one of the most important geochemical phases impacting the mobility and behaviour of metals in sediments (Bilinski et al., 1991; Turner, 2000; Wang et al., 2010). The metal content in this phase has already been proved to be sensitive to anthropogenic inputs (Modak et al., 1992). Metals bound to amorphous Fe oxyhydroxide fraction are unstable under reducing conditions. These conditions result in the release of metal ions to the dissolve fraction. Amorphous Fe oxyhydroxide phase is well recognized for its scavenging properties of metals in the surficial environment and is defined by the extraction with 20 mL of 0.25 M NH₂OH.HCL in 0.25 M HCl and heated for 2 h at 60°C (Hall et al., 1996).

The geochemical fractionation results from the present study are consistent with the high affinity of metals for amorphous oxide minerals. This phase accumulates metals from the aqueous system by the mechanism of adsorption and co-precipitation (Bordas and Bourg, 2001). The relatively higher concentrations of metals such as Ni, Mo, Co and others associated with this fraction are caused by the adsorption of these metals by the Fe-Mn colloids (Purushothaman and Chakrapani, 2007). Industrial discharge may be one of the factors for the increased concentrations of metals in sediments of the study area.

The geochemical fractionation result from the present study revealed the order of affinity of metals as Co > Mo > Ni > Mn > Fe (26.6- 30.5, 23.2- 38.5, 19.0- 40.1, 7.7- 14.7 and 8.3- 13.8% of total, respectively) for amorphous Fe oxyhydroxides of NR sediments (Figure 3). The observed trend in the association of Co, Mo, Ni, Mn and Fe with amorphous Fe oxyhydroxide minerals were moderately well explained and the presence of Fe oxyhydroxide minerals, such as goethite in the samples of NR sediments also detected by the XRD data, which already been published in our previous report (Zakir et al., 2008). The results obtained for the sediments of Nomi river of Tokyo (Sharmin et al., 2010) are also at par with the present study.

Crystalline Fe-oxide fraction

In contrast to amorphous Fe oxyhydroxide, the mean percentage for crystalline Fe oxide fraction was lower for Co and Ni (Figure 3). This is probably due to the much greater surface area of amorphous minerals in comparison with crystalline materials (Kampf et al., 2000;

Zakir et al., 2008). On the other hand, considering the mean percentage only 26.4, 15.7, 10.8, 9.0 and 8.2% of total Mo, Co, Ni, Fe and Mn, respectively were associated with the operationally defined crystalline Fe oxide fraction. It is apparent from the Figure 3 that the association of Fe, Mn and Mo in this fraction was almost similar to the amorphous Fe oxyhydroxide phase. Metals associated with oxide (both amorphous and crystalline) minerals are likely to be released in reducing condition.

However, the affinity order of different metals for crystalline Fe oxide was: Mo > Co > Ni > Fe > Mn. According to Sharmin et al. (2010) the affinity order of trace metals for the same fraction of sediment samples of Nomi river was Cu > Fe > Ni > Cr > Mn.

Fraction bound to organic matters and sulfides

Organic matter and sulphides are important factors controlling the mobility and bioavailability of metals. Current opinions reflects on the toxicity of metals influenced by organic matters (Hoss et al., 2001; Besser et al., 2003). Degradation of organic matter under oxidizing conditions can lead to the release of soluble metals bound to this fraction (Purushothaman and Chakrapani, 2007). The affinity of metals for organic substances and their decomposition products are of great importance for the release of the metals into water. Metal bound to this fraction is assumed to reflect strong association with sediment organic material. The fractionation result from the present study revealed that on an average 22.5, 17.4, 16.9, 12.5 and 14.3% of total Fe, Mn, Co, Ni and Mo, respectively were associated with the sulfides and organic (oxidizable) fraction (Figure 3).

On the other hand, after residual fraction, major association with this fraction was found for Fe and Mn, may be for high affinity with organic matter and also scavenging properties of this fraction. This indicates that Fe and Mn occurred in the form of stable organic complexes and metal sulphides. This result is in good agreement with the literature reported by Prasad et al. (2006) and Sharmin et al. (2010).

Silicate and residual fraction

Silicate and residual fraction of metals are generally much less toxic for organisms in aquatic environment because this fraction is chemically stable and biologically inactive. In the present study residual form was the dominant for Fe and Mn. Fractionation profile of present study indicating average affinities of Fe, Mn, Co, Ni and Mo were 57.5, 49.3, 19.4, 20.9 and 18.2 % of total, respectively for silicate and residual fraction (Figure 3).

The metal present in the residual fraction can be used as a baseline data for the assessment of the degree of contamination of the system. The association between

metals and the residual fraction of uncontaminated soils is so strong that metal association with non-residual fraction has been used as an indicator of anthropogenic enrichment (Sutherland et al., 2000; Zakir, 2008).

Environmental mobility and geochemical partitioning trend of metals

Here, a summary of geochemical partitioning results is described and environmental mobility pattern is assessed for a particular metal. Overall, the order of importance of different geochemical fractions of metals in NR sediment samples obtained for the study were:

- 1) Co: amorphous Fe oxyhydroxide > bound to carbonate > silicates and residual \geq sulphides and organics > crystalline Fe oxide > exchangeable
 - 2) Fe: silicates and residual > sulphide and organics > amorphous Fe oxyhydroxide \geq crystalline Fe oxide > bound to carbonate > exchangeable
 - 3) Mn: silicates and residual > sulphide and organics > bound to carbonate > amorphous Fe oxyhydroxide \geq crystalline Fe oxide > exchangeable
 - 4) Mo: amorphous Fe oxyhydroxide > crystalline Fe oxide > silicates and residual > bound to carbonate > sulphide and organics > exchangeable
 - 5) Ni: amorphous Fe oxyhydroxide > bound to carbonate > silicates and residual > sulphide and organics > crystalline Fe oxide > exchangeable
- These findings suggest that the order of potential mobility of metals in the aquatic environment of the study area is: Ni \geq Co > Mo > Mn > Fe

Assessment of metal pollution in sediments

Normalization of metals

The normalization of the concentrations of metals using Al as a conservative element confirmed that with little exception all the sampling sites are the most polluted by Ni, Mo and Mn (Figure 4). Furthermore, the normalization revealed that all the sampling stations (2- 20) of NR and OR were enriched with Ni, Mo and Mn when the ratios are compared with the baseline values. It is also evident from Figure 4 that the calculated ratios for Fe and Co at all the sampling sites were less or very close to the ratios obtained from the Earth's crust average (Huheey, 1983) data, which have been considered as baseline value indicates the study area is not polluted by Fe and Co.

Risk assessment code (RAC)

The distribution of metal speciation associated with different geochemical fraction is a critical parameter to

assess the potential mobility and bioavailability of metals in sediments. RAC as applied to the present study revealed that on an average 24.4, 19.1, 18.1 and 14.5% of total Ni, Mo, Co and Mn, respectively of the study sites either is adsorb, exchangeable or carbonate bound and therefore comes under the medium risk category to local environment and can easily enter into the food chain (Tables 1 and 2).

Because of the toxicity and availability of metals, they can pose serious problem to the ecosystem, and can be remobilized by changes in environmental conditions such as pH, redox potential, salinity etc. On the other hand, only 0- 0.95% of total Fe was found in the exchangeable and carbonate bound fraction with an average value of 0.32% and therefore comes under the no risk category indicating lower availability from which Fe cannot be easily leached out for the aquatic environment (Tables 1 and 2). So, the potential hazard of Ni, Mo, Co and Mn were larger than those of Fe which occurred mostly in the inert residual fraction.

Geoaccumulation Index (I_{geo})

The calculated index of geoaccumulation (I_{geo}) of the metals in the sediments of NR and their corresponding contamination intensity are shown in Figure 5. The I_{geo} values for Ni ranged from 0.3 to 1.4 corresponded with class 0 to 2, which exhibited unpolluted/ uncontaminated to moderately contaminated sediment quality. Similarly, the I_{geo} values for Mo ranged from 0.2 to 2.8 corresponded with class 0 to 3, which exhibited unpolluted/ uncontaminated and moderately to strongly polluted sediment quality. It is evident from Figure 5 that all the sampling stations of NR and OR are moderately to strongly polluted (class 1-3) for Mo and Ni, but the sampling sites (nos. 1 and 21) of AR were unpolluted (class 0) may be due to higher flow of current and water level.

The results revealed that Ni and Mo contamination of the sediments of NR and OR could have significant impact on aquatic ecology. On the other hand, it is also evident from the Figure 5 that the sediments of the study area are unpolluted with respect to Fe, Mn and Co as the I_{geo} values for those metals were negative in the study sites.

Conclusion

Identification and quantification of metal sources in soil and sediment, as well as the fate of those metals, are important environmental scientific issues. This study has been focused mainly on environmental mobility and geochemical partitioning of Fe, Mn, Co, Ni and Mo in sediment profiles of NR, Tokyo, Japan. The present study also used several tools, methods and indices for the

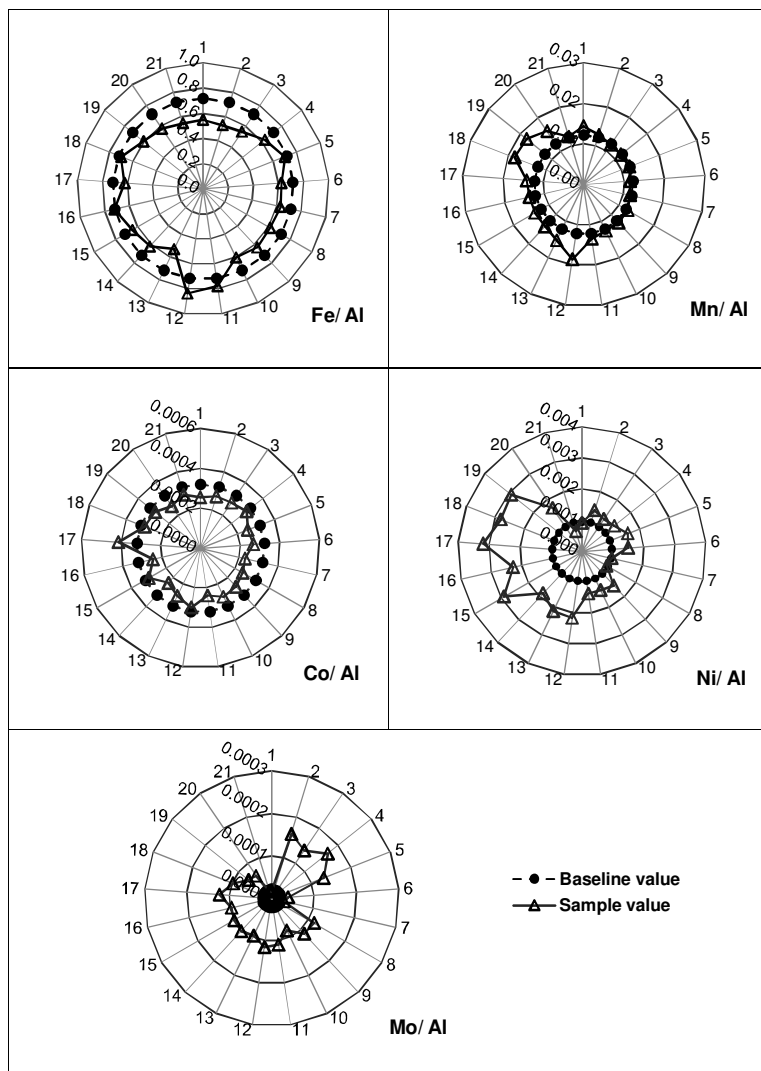


Figure 4. Normalized ratio of Fe, Mn, Co, Ni and Mo among the sampling sites using Al as conservative element. Broken line indicates the Earth's crust average as baseline value.

Table 2. Speciation pattern up to carbonate fraction for Fe, Mn, Co, Ni and Mo in sediments of the sampling sites and risk assessment code (RAC).

Metal	Average percentage in each fraction (in % of total)			Level of risk on the basis of RAC
	Exchangeable	Bound to carbonates	Total in both fraction	
Fe	0.18	0.14	0.32	No risk
Mn	3.4	11.1	14.5	Medium risk
Co	0.0	18.1	18.1	Medium risk
Ni	2.3	22.1	24.4	Medium risk
Mo	2.6	16.5	19.1	Medium risk

evaluation of sediment quality, which provides valuable information for decision-making processes and management involving natural resources. However, a

detailed examination on geochemical partitioning and normalization results indicate that Ni and Mo are anthropogenically enriched in sediments of NR, which

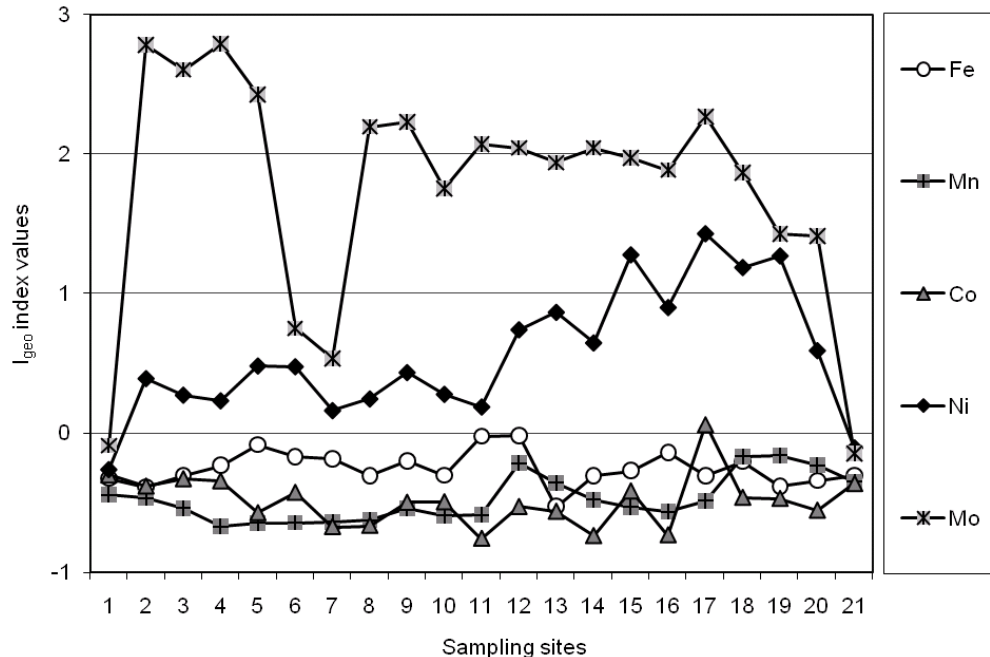


Figure 5. Geoaccumulation index (I_{geo}) of Fe, Mn, Co, Ni and Mo in sediment samples at different sampling sites of the study area.

has much effect on environment and humans.

According to geoaccumulation index, Ni and Mo also exhibited uncontaminated to strongly polluted sediment quality. On the other hand, residual and silicate fraction was the main geochemical association for Fe, Mn and Co, which has little effect on environment suggesting weak pollution risk. RAC as applied to the present study revealed that except Fe, all other metals comes under the medium risk category to local environment. However, the lower mean percentage of active fractions is an advantage to control the environmental pollution in the study sites.

REFERENCES

- Amiard JC, Geffard A, Amiard-Triquet C, Couzet C (2007). Relationship between the lability of sediment-bound metals (Cd, Cu, Zn) and their bioaccumulation in benthic invertebrates. *Estuar. Coast. Shelf Sci.*, 72: 511-521.
- Badr NBE, El-Fiky AA, Mostafa AR, Al-Mur BA (2009). Metal pollution records in core sediments of some Red Sea coastal areas, Kingdom of Saudi Arabia. *Environ. Monit. Assess.*, 155: 509-526.
- Basta N, Gradwohl R (2000). Estimation of Cd, Pb and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure. *J. Soil Contam.*, 9: 149-164.
- Besser JM, Brumbaugh WG, May TW, Ingersoll CG (2003). Effects of organic amendments on the toxicity and bioavailability of cadmium and copper in spiked formulated sediments. *Environ. Toxicol. Chem.*, 22: 805-815.
- Bilinski H, Kozar M, Plavsic, Kwokal Z, Branica M (1991). Trace metal adsorption on inorganic solid phases under estuarine conditions. *Mar. Chem.*, 32: 225-233.
- Bordas F, Bourg A (2001). Effect of solid/liquid ratio on the remobilization of Cu, Pb, Cd and Zn from polluted river sediment. *Water Air Soil Pollut.*, 128: 391-400.
- Datta DK, Subramanian V (1998). Distribution and fractionation of heavy metals in the surface sediments of the Ganges-Brahmaputra-Meghna river system in the Bengal basin. *Environ. Geol.*, 36(1-2): 93-101.
- Hall GEM, Vaive JE, Beer R, Hoashi M (1996). Selective leaches revisited, with emphasis on the amorphous Fe oxyhydroxide phase extraction. *J. Geochem. Explor.*, 56: 59-78.
- Hickey MG, Kittrick JA (1984). Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.*, 13: 372-376.
- Horowitz AJ (1991). *A Primer on Sediment- Trace Element Chemistry*. 2nd edition, Lewis Publishers, Chelsea (Michigan), p.136
- Hoss S, Henschel T, Haitzer M, Traunspurger W, Steinberg CEW (2001). Toxicity of cadmium to *Caenorhabditis elegans* (Nematoda) in whole sediment and pore water – The ambiguous role of organic matter. *Environ. Toxicol. Chem.*, 20: 2794-2801.
- Huheey JE (1983). *Inorganic Chemistry: Principle of Structure and Reactivity*. Harper and Row Publisher, New York, p.912
- Jain CK (2004). Metal fractionation study on bed sediments of River Yamuna, India. *Water Res.*, 38: 569-578.
- Kampf N, Scheinost AL, Schulze DG (2000). Oxide Minerals. In: Sumner ME (ed.) *Handbook of Soil Science*. CRC Press, Boca Raton, FL. pp. 125-168.
- Liu WX, Li XD, Shen ZG, Wang DC, Wai OWH, Li YS (2003). Multivariate statistical study of heavy metal enrichment in sediment of the Pearl River Estuary. *Environ. Pollut.*, 121: 377-388.
- Milacic R, Scancar J, Murko S, Kocman D, Horvat M (2010). A complex investigation of the extent of pollution in sediments of the Sava River. Part 1: Selected elements. *Environ. Monit. Assess.*, 163: 263-275.
- Modak DP, Singh KP, Chandra H, Ray PK (1992). Mobile and bound form of trace metals in sediments of the lower Ganges. *Water Res.*, 26(11): 1541-1548.
- Morillo J, Usero J, Gracia I (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, 55(3): 431-442.
- Muller G (1969). Index of geoaccumulation in sediments of the Rhine River. *Geo. J.*, 2(3): 108-118.

- Omori M, Hatayama Y, Horiguchi M (Eds.) (1986). *Geology of Japan, Kanto Districts* (in Japanese). 1st ed., Kyooritsu Publishing Co., Tokyo, Japan, p.350
- Pardo R, Barrado E, Perez L, Vega M (1990). Determination and association of heavy metals in sediments of the Pisucraga, river. *Water Res.*, 24(3): 373-379.
- Perin G, Craboledda L, Lucchese M, Cirillo R, Dotta L, Zanetta ML, Oro AA (1985). Heavy metal speciation in the sediments of northern Adriatic sea. A new approach for environmental toxicity determination. In: Lakkas TD (Ed.). *Heavy Metals in the Environment*, CEP Consultants, Edinburgh. 2: 454-456.
- Prasad MBK, Ramanathan AL, Shrivastav SKR, Anshumali, Saxena R (2006). Metal fractionation studies in surficial and core sediments in the Achankovil river basin in India. *Environ. Monit. Assess.*, 121: 77-102.
- Pueyo M, Sastre J, Hernandez E, Vidal M, Lopez-Sanchez JF, Rauret G (2003). Prediction of trace element mobility in contaminated soils by sequential extraction. *J. Environ. Qual.*, 32: 2054-2066.
- Purushothaman P, Chakrapani GJ (2007). Heavy metals fractionation in Ganga river sediments, India. *Environ. Monit. Assess.*, 132: 475-489.
- Sharmin Shaila, Zakir HM, Shikazono Naotatsu (2010). Fractionation profile and mobility pattern of trace metals in sediments of Nomi River, Tokyo, Japan. *J. Soil Sci. Environ. Manag.*, 1: 1-14.
- Singh KV, Singh PK, Mohan D (2005). Status of heavy metals in water and bed sediments of river Gomti- a tributary of the Ganga River, India. *Environ. Monit. Assess.*, 105: 43-67.
- Sutherland RA, Tack FMG, Tolosa CA, Verloo MG (2000). Operationally defined metal fractions in road deposited sediment, Honolulu, Hawaii. *J. Environ. Qual.*, 29: 1431-1439.
- Takesako H, Wada N, Sumida H, Kawahigashi M, Miyamoto J, Suzuki S, Tanaka H, Yokotagawa T, Inubushi K (2002). Properties of soil in Chiba University's Atagawa Farm. III. Mineralogical properties and soil classification of volcanic ash soils (in Japanese). *Chiba University, Tech. Bull. Fac. Hort.*, 56: 27-37.
- Tessier A, Campbell PGC, Bisson M (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51(7): 844-851.
- Turekian KK, Wedepohl KH (1961). Distribution of the elements in some major units of the earth's crust. *Geol. Soc. Am. Bull.*, 72: 175-192.
- Turner A (2000). Trace metal contamination in sediments from U.K. estuaries: an empirical evaluation of the role of hydrous iron and manganese oxides. *Estuar. Coast. Shelf Sci.*, 50: 355-371.
- Turner A, Olsen YS (2000). Bioavailability of trace metal in contaminated estuarine sediments: A comparison of chemical and enzymatic extractants. *Estuar. Coast. Shelf Sci.*, 51: 717-728.
- USAMS (US Army Map Service) (1945-46). US Army map service city plans for the Tokyo area. Sheet 9- Honjo. Reproduced from compilation manuscript by overprints. UT Library online, http://www.lib.utexas.edu/maps/ams/japan_city_plans/index_tokyo.html
- Wang S, Jia Y, Wang S, Wang X, Wang H, Zhao Z, Liu B (2010). Fractionation of heavy metals in shallow marine sediments from Jinzhou Bay, China. *J. Environ. Sci.*, 22(1): 23-31.
- Zakir HM (2008). Geochemical partitioning of trace metals: an evaluation of different fractionation methods and assessment of anthropogenic pollution in river sediments. Ph D thesis, Keio Univ. Yokohama, Japan. pp. 1-156
- Zakir HM, Shikazono N (2008). Metal fractionation in sediments: a comparative assessment of four sequential extraction schemes. *J. Environ. Sci. Sustainable Soc.*, 2: 1-12.
- Zakir HM, Shikazono N, Otomo K (2008). Geochemical distribution of trace metals and assessment of anthropogenic pollution in sediments of Old Nakagawa River, Tokyo, Japan. *Am. J. Environ. Sci.*, 4(6): 661-672.