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Full Length Research Paper

Fractionation profile and mobility pattern of trace metals in sediments of Nomi River, Tokyo, Japan

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This study provides a geochemical partitioning and mobility pattern of Iron (Fe), Manganese (Mn), Cadmium (Cd), Copper (Cu), Chromium (Cr) and Nickel (Ni) in sediment samples collected from Nomi River, Tokyo, Japan. For the partitioning of particulating trace metals, a widely used 5-step sequential extraction procedure was employed and the concentrations were measured in the liquid extracts by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Absorption Spectroscopy (AAS) to understand enrichment and metal availability in five geochemical phases. The association of Cd (39.8-89.7%) was found highest with adsorbed, exchangeable and carbonate (AEC) fraction, Fe (25 - 44.1%), Mn (11.8 - 76.7%), Cr (12.6 - 46.9%) and Ni (9.8 - 41.8%) were in residual phase and the maximum association of Cu was recorded with amorphous Fe Oxyhydroxide phase (24.7 - 51.3%). The order of potential trace metals mobility in the aquatic environment of Nomi River was- Cd > Cu > Cr > Ni > Fe > Mn. According to the risk assessment code applied in the present study Cu, Ni and Cr were under medium and Cd was under high risk category. The X-ray diffraction (XRD) study detected the presence of several clay minerals; those are likely to be the major host of trace metals in sediments.

Key words: Trace metal, fractionation, mobility, pollution, sediments, Nomi River, Tokyo.

INTRODUCTION

Due to rapid expansion of Ota Ward, Tokyo, Japan more waste products have been discharged from municipalities, industries and spilled into water ways (OCIPO, 2007). Much concern has been focused on the investigation of the total metal contents in sediments. The result from the determination of trace metals in sediments reflects the impacts of industrial activities and urban development (Fang and Li, 2005). Trace metals are not fixed permanently in the sediment and may be recycled via biological and chemical agents both within the sedimentary compartment and water column. In general, the environmental risk arising from metal contamination in river sediments cannot be assessed only on the basis of total contents but needs to consider also the forms in which they are associated with sediment. Today it is generally recognized that the particular behavior of trace metals in the environment is determined mostly by their specific physicochemical fractionation and speciation or chemical form rather than by their total concentration (Tack and Verloo, 1995), and therefore, speciation studies increasingly gain importance (Liu et al., 2007; Zakir and Shikazono, 2008).

There are a wide variety of sequential extraction procedures available in literature based on a different sequence of extractants and/or different operating conditions (Zakir and Shikazono, 2008). Among those, the 4-step SM&T (formerly BCR scheme, modified by Rauret et al., 1999) and the 5- step (Tessier et al., 1979) schemes are most applied. In the Hall scheme (Hall et al., 1996), the oxide/ reducible phase is divided into metals associated with amorphous Fe oxyhydroxide and crystalline oxides of Fe. However, in sequential extraction procedures, four to eight extractants are usually employed in an order in which the earlier ones are the least aggressive and the most specific, and subsequent extractants

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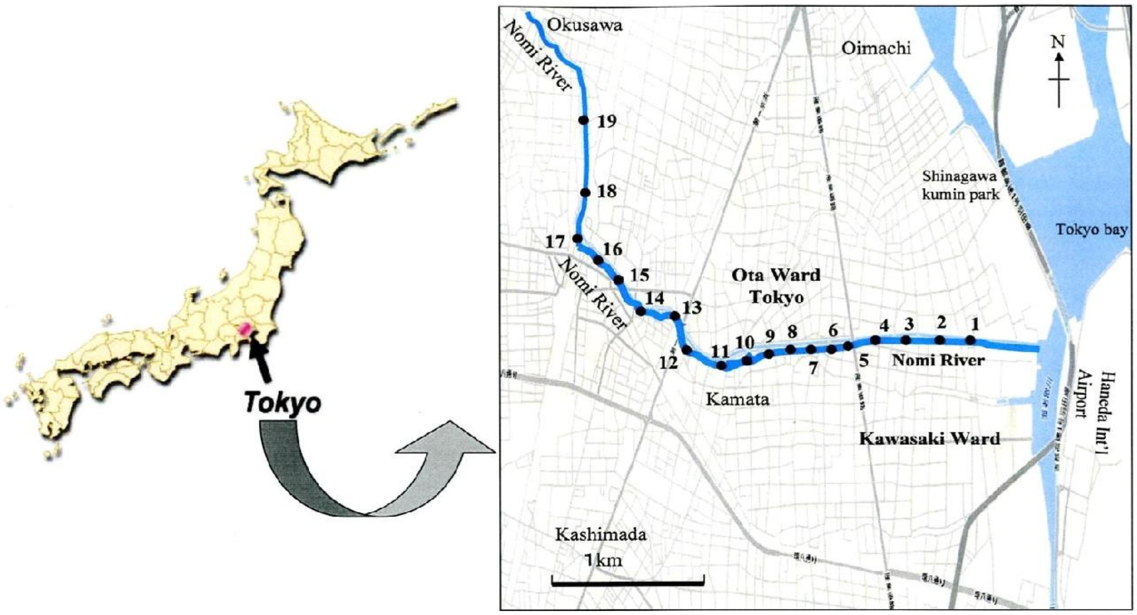

Figure 1. Location of the sampling sites in Nomi River in Tokyo, Japan.

extractants are progressively more destructive and less specific. It is generally assumed that the availability of the metals to the living organisms follows a decreasing order from the first step towards the last step in a sequential extraction scheme.

Nomi River, Tokyo receives significant amount of waste from surrounding industrial and residential area. As far we know, the geochemical studies and literature on the characterization of the sediment of Nomi River, on one of the major urban center like Ota Ward, Tokyo, Japan is currently lacking and there is no systemic research report about trace metal status that's why an attempt has been made to establish existing pollution by emphasizing metal geochemical association status of this river. Although Nomi River is not so big river in comparison to the other Japanese rivers, may be the enrichment of trace metal in some fraction specially in mobile fraction will be emphasized the greater role of the small rivers in modifying the global budget of trace metal to the world ocean. The present study was evaluating the geochemical distribution of Cd, Cu, Ni, Cr, Fe and Mn in sediments taken from Nomi River which has been mainly affected/associated by industrialization, urbanization and technogenic impact/ anthropogenic activities as the industrial sector is a major contributor to environmental pollution. Therefore, the main objective of this work was the assessment of trace metal (Fe, Mn, Cd, Cu, Cr and Ni) speciation as well as the measurement of their mobility pattern in sediments of Nomi River. Finally, the data presented in this study is the only database available for the speciation of metals in the sediments of Nomi River that will certainly help in better resource management of this river basin in future.

General description of the study area

Ota city is largely characterized by the integration of a wide range of industries within an urban setting, mixing factories with residence in addition to an exclusively industrial reclaimed area. The total area is 59.46 km^2 ranking Ota city first among the 23 districts of Tokyo (OCIPO, 2007). Integration of metal processing related factories is observed in the areas along Tokyo Bay, such as Omori Nishi, Omori Minami, Higashi Kojiya and Haneda. The area mainly consists of tertiary and quaternary sedimentary rocks (shale and sandstone) overlain by quaternary materials and weathered soils of volcanic origin. Alluvium sediments consisting of various rock fragments (granite, basalt, chert, limestone, shale, sandstone) were derived from upper stream region where Paleozoic rocks are distributed (Omori et al., 1986). Location of the sampling sites is shown in Figure 1.

MATERIALS AND METHODS

Sample collection and preparation

A total of 19 sediment samples were collected from different location of Nomi River, Tokyo, Japan on March 9, 2008 (Table 1). The sampling distance from one station to another was at least about 100m. The surface sediment samples were taken from 0 - 10 cm depth by using a "bed material sampler" 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 48 h and sieved (aperture 125 m). Then stone and plant fragments were removed. In order to normalize the variations in grain size, the lower particle size fraction was homogenized by grinding in an agate mortar and stored in glass bottles until the se-

Table 1. Location of different sampling sites of Nomi River, Tokyo, Japan.

Site	Location	Site	Location
1	Higashi kaujiya	11	Tenjin bridge
2	Ashahi bridge	12	Metro bridge
3	Toube bridge	13	Dansei bridge
4	Suehiro bridge	14	Yangi bridge
5	Azuma bridge	15	Nakano bridge
6	Nomigawashin bridge	16	Ayami bridge
7	Hatchiman bridge	17	Onari bridge
8	Kitakoujiya bridge	18	Miyano bridge
9	Houri bridge	19	Umahiki bridge
10	Shimizo bridge		

quential extraction analysis were carried out. All chemicals and reagents were of analytical reagent grade quality (Sigma-Aldrich, USA and Wako, Japan). Millipore water was used through all the experiments. Before use, all glass and plastic ware were soaked in 14% HNO_3 for 24 h. The washing was completed with Millipore water rinse.

Sequential extraction experiment

There are wide varieties of sequential extraction procedure available in literature based on a different sequence of extractants and/or different operating condition. Recently, Zakir and Shikazono (2008) conducted a comparative assessment of four commonly used sequential extraction procedures for trace metal partitioning in different types of sediments and reported that Hall scheme (Hall et al., 1996) recovered the maximum metal content. This study was also employed the same scheme and the trace metals were measured in the liquid extract by ICP-MS (Hewlett-Packard 4500, USA) (Cu, Cd, Cr and Ni) and AAS (Hitachi Z-6100) (Fe and Mn). During extraction extractant quality, especially the required pH was maintained carefully. After each step, the solution was filtered by suction through a 0.45 m millipore filter and the filtrate was collected in a polyester container. Then the solutions for each step were prepared accordingly for ICP-MS and AAS measurement following the manufacturer's recommendations. Multielement standard solution (Wako, Japan) was used for the calibration of standard line. A certified reference stream sediment Jsd-2, provided by the Geological Survey of Japan was also analyzed using the same procedure as check and reached 90 - 103 % recovery for the trace metals. All the operations were carried out in 50 ml poly-propylene centrifuge tubes (Nalgene, New York) and Teflon (PTFE) containers provided with screw stoppers. As a quality assurance measure, each sediment sample was subjected to triplicate analysis and the measurements are given as mean, unless noted.

Major elemental constituents and mineralogy of sediments

A preliminary determination of major elements of the samples was carried out by X-ray Fluorescence Spectroscopy (XRF) (Rigaku RIX 1000, Tokyo, Japan). For the preparation of bead, exactly 0.4 g dry oxidized (at 900°C for 14 h) samples; lithium tetraborate (4.0 g) and lithium iodide (50 mg) were mixed together and used a bead sampler (NT 2100, Tokyo, Japan). Plate calibration was performed using standards of Geological Survey of Japan (JB-3, JF-1, JG-2, JGb-2, JH-1 and JSy-1) following the manufacturer's recommendations. The result calculated considering the loss on ignition and express in mass percent. The analytical recoveries for the major elements from Jsd- 2 ranged 94 - 106%. For determination of mineralogy of sediment a Bruker AXS: D-8 Advance (Berlin, Germany) X-ray diffractometer was employed for XRD analysis.

RESULT AND DISCUSSION

The concentrations of major components of sediment samples

The concentrations of major components of sediment samples expressed as oxide are listed in Table 2. It is notable from the Table 2 that oxides of Si, Ti, Mn and K in sediment samples did not vary greatly among the sampling sites of the study area, but oxides of Fe, Al, Ca, Na and P content varied significantly from one to another sampling site. The highest concentrations of Fe, Al, Na and P were recorded in the sampling sites 1, 6, 8, 9 and 14. However, major component concentration suggest, besides the obvious presence of silica, other aluminosilicate minerals, as well as the presence of Fe oxides and to a lesser extent, manganese, titanium and phosphorus containing mineral phases, this result is at par with the findings reported by Zakir et al. (2008) who analyzed river sediment samples of Old Nakagawa River in Tokyo.

Mineralogy of the sediment samples

Mineralogy of sediment samples is a significant factor controlling mobility and dispersion of trace metals in a river system. Mineralogical analysis of all sediment samples collected from Nomi River is shown in Table 3. A predominant mineral composition of the sediments was quartz, which had the strongest peak with the relative intensity of 100. However, other common minerals were feldspar, goethite, calcite, montmorillonite and several clay minerals such as chlorite, chamosite, kaolinite and muscovite. It is worth mentioning that the presence of iron oxides and hydroxide group minerals, specifically goethite as detected in most of the sampling sites. The mineral composition of all the samples agreed qualita-tively with the concentrations of major components of

Table 2. The concentrations of major components of sediment samples expressed as oxides (mass %) present in sediments of Nomi River, Tokyo, Japan.

Sampling sites	The concentration of major components of sediment samples (mass %)										Total	LOI (%)
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5		
1	60.1	0.81	17.0	7.8	0.08	2.58	2.69	4.84	2.5	0.42	98.9	19.0
2	70.2	0.58	13.1	5.9	0.09	2.09	2.54	3.01	2.1	0.20	99.7	6.1
3	70.1	0.58	13.1	5.7	0.08	1.95	2.73	2.74	2.0	0.19	99.1	8.0
4	71.1	0.50	13.1	5.1	0.07	1.63	2.44	2.68	2.1	0.16	98.8	6.6
5	74.1	0.52	11.9	4.9	0.08	1.62	1.96	2.52	1.9	0.10	99.7	4.1
6	57.8	0.83	16.0	7.6	0.08	2.53	2.63	4.31	2.2	0.40	94.4	17.7
7	74.0	0.48	12.1	4.8	0.08	1.59	1.81	2.48	2.0	0.10	99.4	4.6
8	61.8	0.75	15.6	9.5	0.11	2.17	2.53	3.49	2.1	0.36	98.4	14.1
9	66.3	0.68	14.3	6.8	0.10	2.30	3.14	3.12	1.7	0.34	98.8	9.4
10	70.0	0.57	13.6	5.8	0.09	1.80	2.56	2.72	1.9	0.17	99.3	6.3
11	73.8	0.43	12.4	4.6	0.07	1.68	2.62	2.52	1.8	0.07	100.1	3.1
12	74.9	0.44	10.9	5.2	0.09	2.04	2.44	2.26	1.6	0.11	100.0	4.8
13	71.3	0.63	14.0	5.6	0.08	1.32	1.18	2.43	2.2	0.11	98.8	4.8
14	61.5	0.81	17.5	8.0	0.10	2.39	2.39	3.63	2.0	0.53	98.8	14.2
15	75.0	0.43	10.7	5.1	0.09	2.03	2.36	2.37	1.6	0.06	99.7	2.8
16	73.0	0.45	10.8	5.9	0.12	2.97	3.05	2.19	1.5	0.05	100.0	1.8
17	75.4	0.40	10.6	5.0	0.09	2.1	2.54	2.15	1.5	0.07	99.9	1.8
18	77.1	0.36	9.5	4.7	0.09	1.96	2.26	2.01	1.4	0.05	99.5	2.3
19	71.5	0.53	10.1	7.0	0.14	3.45	3.58	2.02	1.3	0.07	99.7	2.8
JRS* (average)	--	0.77	10.86	6.13	0.12	2.82	2.52	2.16	1.73	0.13	--	--

LOI= Loss on ignition; JRS= Japanese river sediment; *(Gamo, 2007).

sediments samples determined by XRF (Table 2).

Geochemical fractionation profile of trace metals

Metal partitioning among sedimentary organic and mineral components as well as the physicochemical mechanisms of trace metals enrichment both remain as important research areas. In sediment, trace metals can be present in a number of chemical forms, and generally exhibit different physical and chemical behavior in terms of chemical interaction, mobility, biological availability and potential toxicity. 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. The major mechanisms of accumulation of trace metals in sediment lead to the existence of five categories; exchangeable, bound to carbonate, bound to reducible phases (iron and manganese), bound to organic matter and residues (Singh et al., 2005). These categories have different behaviors 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). The following sections describe trace metal phase distributions

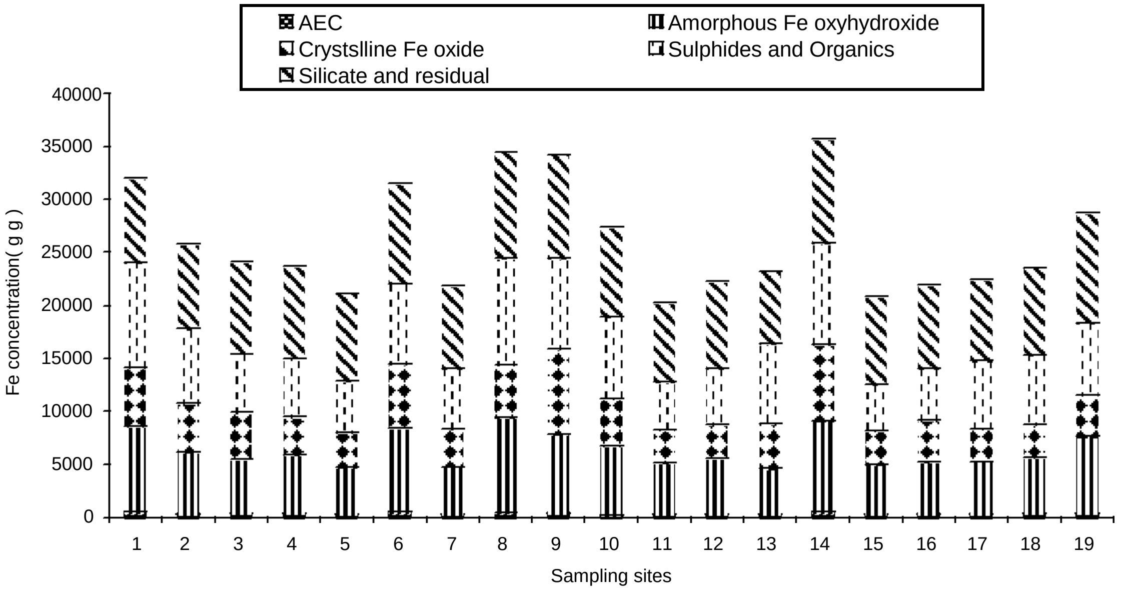

Figure 2. Geochemical distribution of Fe concentration (μg g^{-1}) in sediment samples at different sampling sites of the study area.

according to the sequential extraction procedure applied in this study.

Fraction 1 (AEC-adsorbed /exchangeable/carbonate)

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). For 1 gm sediment the extractant used for this fraction was 20 ml of 1 M sodium acetate (NaOAc) (pH = 5 adjusted with acetic acid) and then 6 h stirring and then centrifugation. Preferential association of AEC bound Cd (39.78 - 89.71% of total) was found in Nomi River sediments (Figure 4). The major fraction of cadmium in carbonate form would imply that an appreciable percentage of cadmium becoming readily available following a slight lowering of pH (Jain, 2004; Zakir et al., 2008). Trace 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 presented in Table 3 also indicate presence of higher amount of carbonate and several clay minerals in Nomi River sediments, which support these findings. However trace 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). Trace metals in this fraction are adsorbed on sediments or on their essential components namely clays, Fe and Mn hydrated oxides and humic acids. The adsorption of trace metals is related to changes in water ionic strength that this fraction could be regarded as a pollution indicator (Zakir, 2008). Turner and Olsen (2000) determined extractability of trace metals in contaminated 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 (Tessier and Campbell, 1987). Finally association of Cd with this fraction is probably the best example of human-induced influence in the sediments of Nomi River, which was in good agreement with the data reported by Zakir et al. (2008). However the AEC fractions recovered for Fe, Mn, Cu, Ni and Cr in sediments of Nomi River were comparatively low (0.57 - 1.57, 0.66 - 4.11, 8 - 19.4, 0.60 - 20.06 and 5.63 - 26.52%, respectively), suggesting lower pollution risk (Figures. 2, 3, 5 - 7).

Fraction 2 (Amorphous Fe oxyhydroxide)

This fraction is also known as the reducible phase. The trace metal content in the Fe/Mn oxide phase which has been proved to be sensitive to anthropogenic inputs (Modak et al., 1992). Metal bound to Fe- Mn oxide 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 trace metals in the surficial environment and is defined by the extraction with 20 ml of 0.25 M NH$_2$OH.HCL in 0.25 M HCl and heated for 2 h at 60°C (Hall et al., 1996). In comparison with carbonate minerals amorphous oxide minerals have relatively large

Table 3. Mineralogical constituents of sediment samples collected from the sampling sites of Nomi River, Tokyo, Japan.

Minerals	Angle (2)	d- value (Å)	Peak intensity range (%)
Quartz	26.63	3.35	100
	20.84	4.26	19-28.5
	50.11	1.81	8.6-17.1
Feldspar	27.73	3.21	8.3-18.9
	27.44	3.24	4.2-10.8
	27.94	3.19	16.3-22.2
	21.99	4.04	4.6-11.7
	23.56	3.75	3.8-12
	24.24	3.67	3.1-11.4
	25.54	3.48	2.8-10.1
Feldspar/chlorites	31.69	2.82	2.7-22.3
Chamosite	12.46	7.09	3.4-12
Chlorites	25.15	3.53	2.6-10.3
	18.79	4.71	2.8-8.9
Muscovite	34.94	2.57	2.6-9.8
Goethite	37.02	2.43	3-9
Calcite	29.42	3.03	2.9-10
	47.15	1.92	2.4-7.6
Kaolinite	45.76	1.98	4.3-9.5
	39.46	2.28	5.9-12.3
Montmorillonoids	19.77	4.48	3-10.8
	34.56	2.59	2.3-7.6

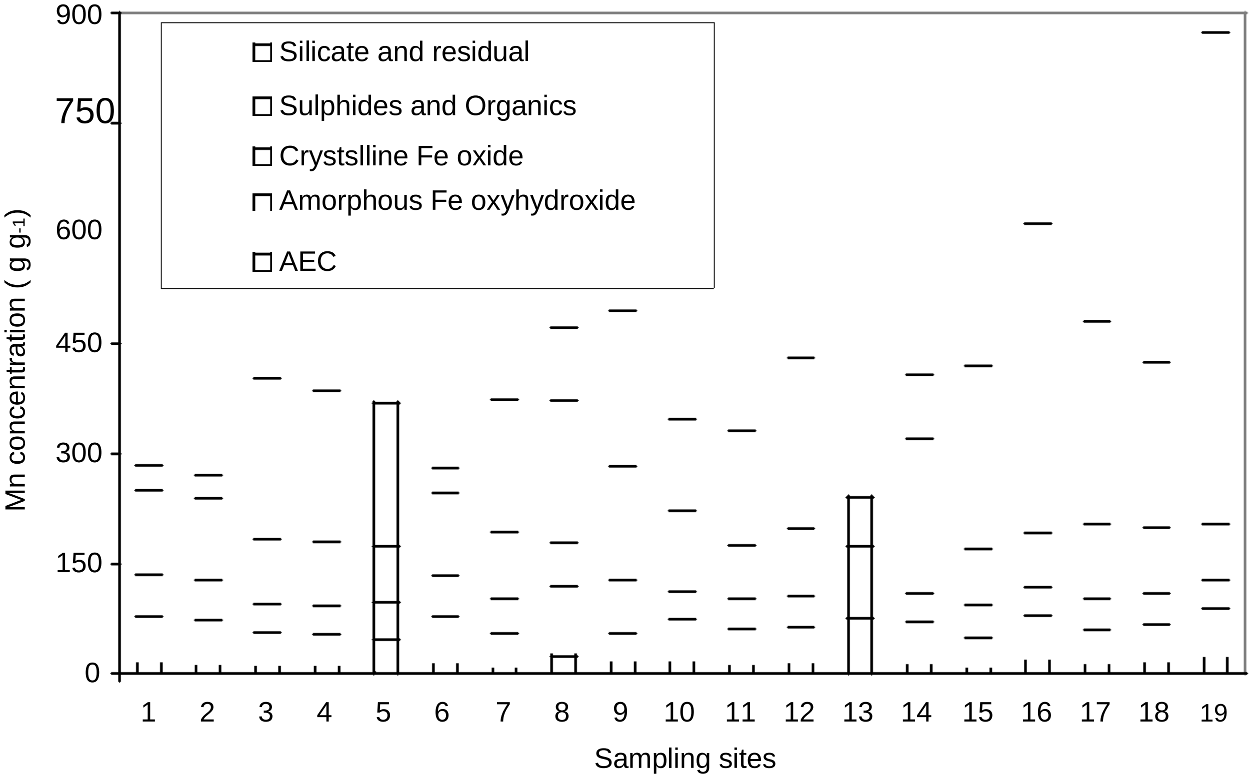

Figure 3. Geochemical distribution of Mn concentration (µg g^{-1}) in sediment samples at different sampling sites of the study are

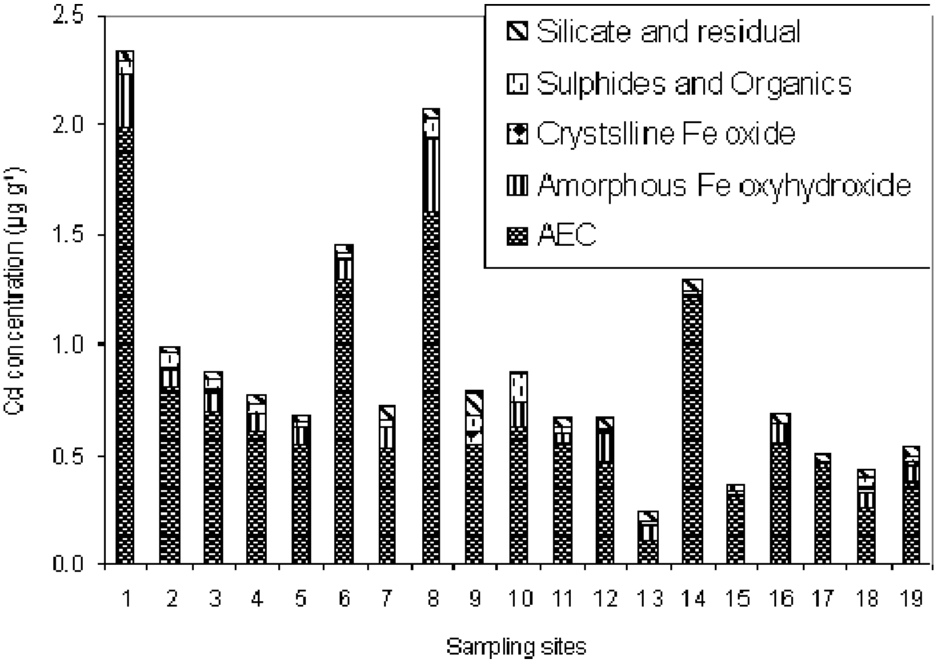

Figure 4. Geochemical distribution of Cd concentration (µg g^{-1}) in sediment samples at different sampling sites of the study area.

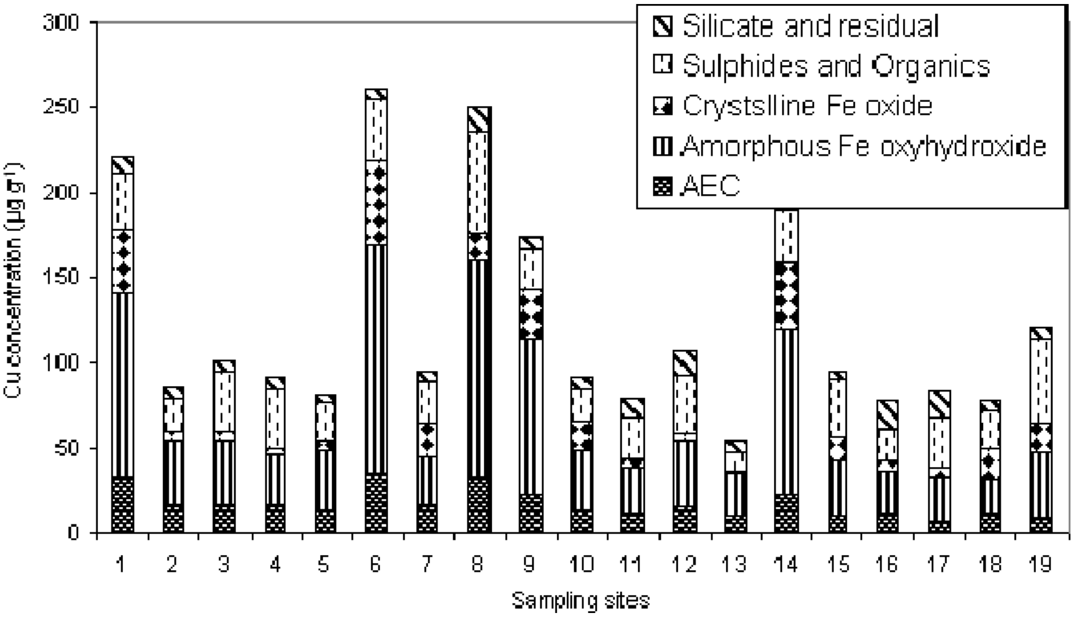

Figure 5. Geochemical distribution of Cu concentration (µg g^{-1}) in sediment samples at different sampling sites of the study area.

surface area and surface site density (Bilinski et al., 1991). The geochemical fractionation results from the present study are consistent with the high affinity of trace metals for amorphous oxide minerals. The Fe and Mn hydroxide constitutes a significant sink for trace metal in the aquatic system. This phase accumulates metals from the aqueous system by the mechanism of adsorption and co-precipitation (Bordas and Bourg, 2001). The relatively

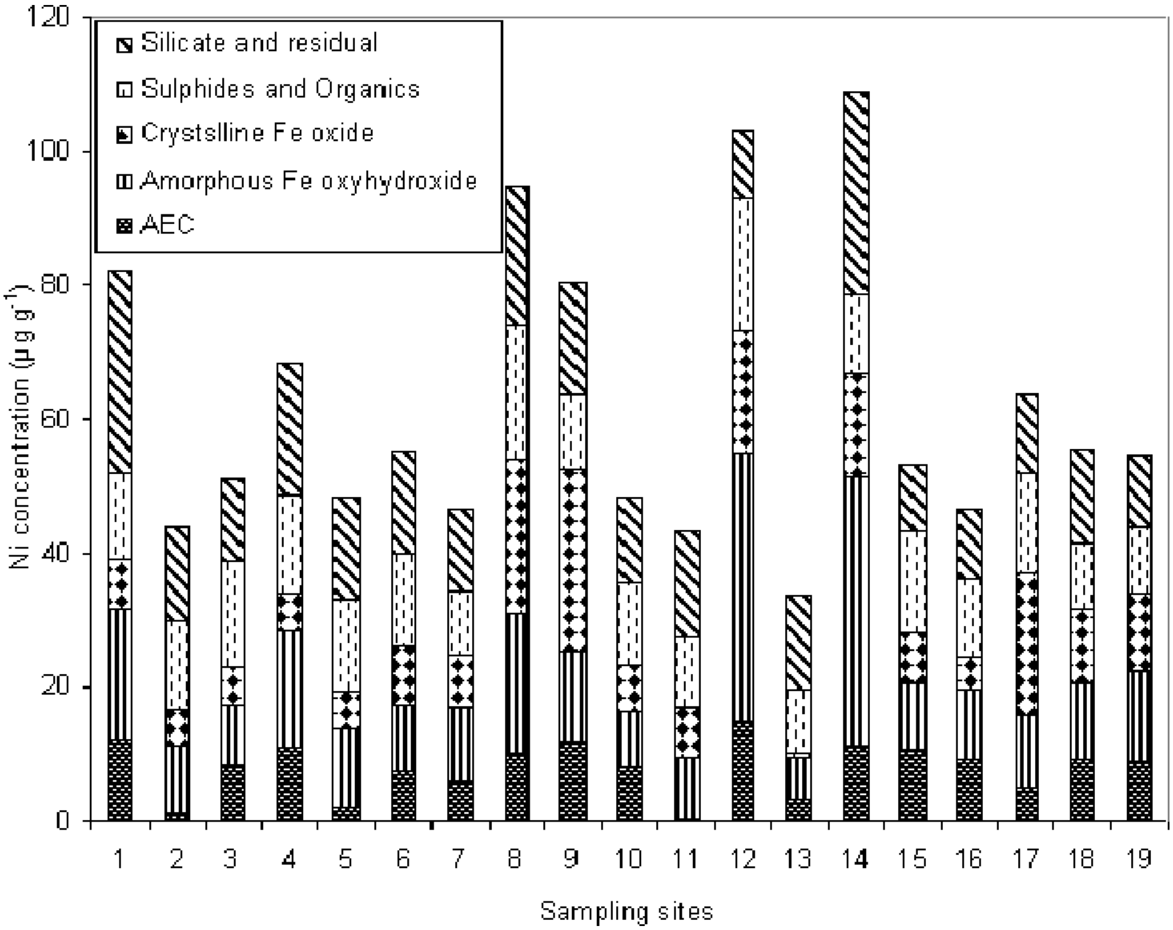

Figure 6. Geochemical distribution of Ni concentration (µg g^{-1}) in sediment samples at different sampling sites

higher concentrations of elements such as Fe, Mn, Cd, Pb, Cu, Zn, Cr, Ni, etc. 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 these metals in Nomi River systems. The geochemical fractionation result from the present study found relatively high affinity of Cu (24.7 - 51.3% of total), Fe (18.8 - 30.6% of total), Mn (6.6 - 23.6% of total), Cd (0 - 23.03% of total), Ni (16.5 - 38.6% of total) and Cr (8.98 - 31.62% of total) for amorphous Fe oxyhydroxide minerals of Nomi River sediments (Figures 2 - 7). The observed trend in the association of Cr, Cu, Ni, Mn, Fe and Cd with amorphous Fe oxyhydroxide minerals were moderately well explained and the presence of Fe oxyhydroxide minerals, such as goethite in the samples of Nomi River also detected by the XRD data (Table 3), which are in good agreement with the literature data proposed by Zakir et al. (2008). Our result are substantiated by the fact that Cu was expected to be associated with large surface area of amorphous Fe oxyhydroxide mineral either by co-precipitation or by sorption onto preexisting coatings under existing physic-chemical conditions (Panda et al.,1995). For retention by the amorphous Fe oxyhydroxide minerals the observed stoichiometric gradient was 3.25 for Fe, 1.67 for Cu, 2.03 for Ni, 3.38 for Cr and 2.75 for Mn (Table 4). In terms of the stoichiometric affinity of different trace metals for amorphous Fe oxyhydroxide, the affinity order was- Cr > Fe > Mn > Ni > Cu.

Fraction 3 (Crystalline Fe oxide)

In contrast to amorphous minerals, the mean percentage for crystalline Fe oxide fraction was lower for Fe, Mn, Cu, Cd, Ni and Cr (Figures. 2-7). This probably reflects 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 16.8% of total Fe, 12.4% of total Cd, 11.6% of total Cu, 16.1% of total Ni and 17.6% of total Cr were associated with the operationally defined crystalline Fe oxide fraction (Figures. 2 - 7). It is apparent

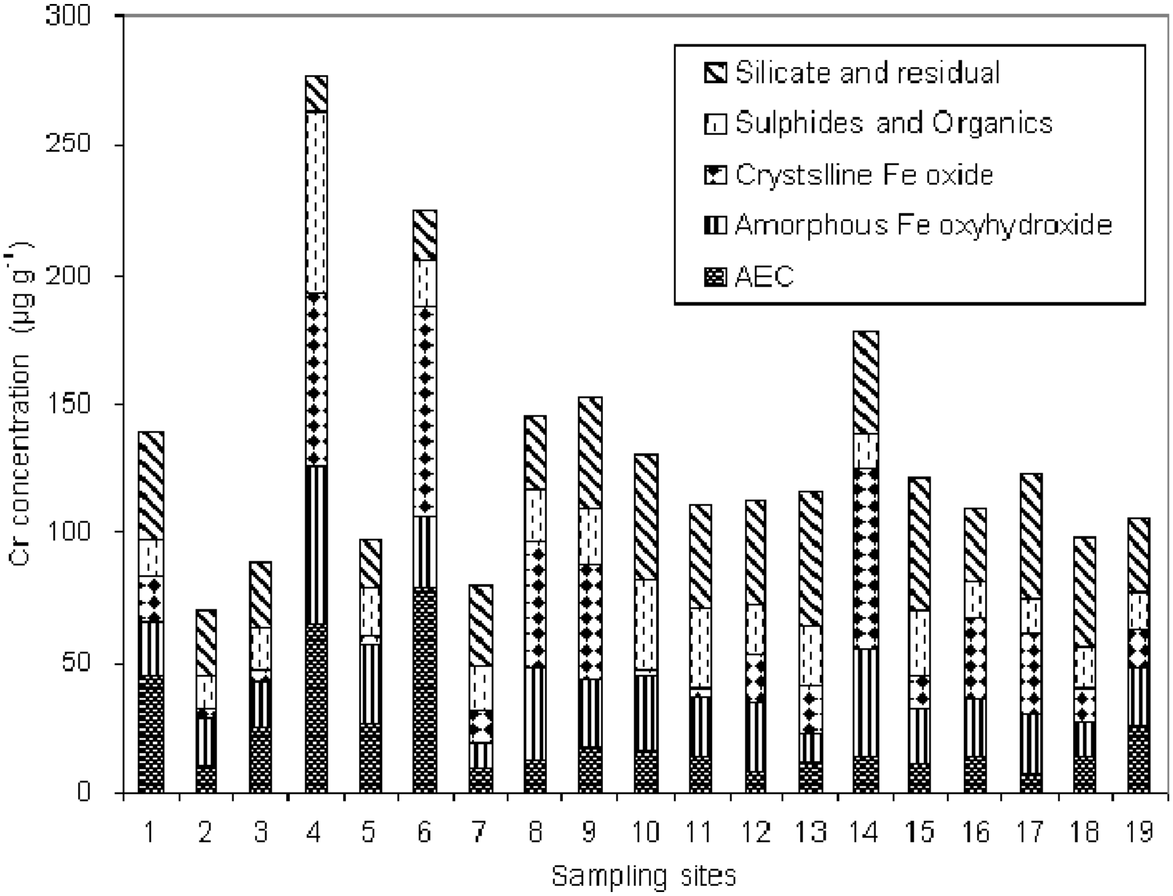

Figure 7. Geochemical distribution of Cr concentration (µg g^{-1}) in sediment samples at different sampling sites of the study area.

from the Figure. 7 that the association of Cr in this fraction was almost similar to the amorphous Fe oxyhydroxide phase (19.6%). For retention by Fe oxide minerals, the observed stoichiometric gradient was: 3.12 for Fe, 3.82 for Cu, 2.11 for Ni, 1.74 for Cr and -4.07 for Mn, and the values were lower than amorphous Fe oxyhydroxide fraction for Fe and Cr (Table 4), indicating crystalline oxide minerals have less stoichiometric affinity for these metals than do amorphous oxyhydroxide minerals. Trace metals associated with oxide (both amorphous and crystalline) minerals are likely to be released in reducing condition. However, the affinity order of different trace metals for crystalline Fe oxide was- Cu > Fe > Ni > Cr > Mn.

Fraction 4 (Sulphides and organics)

The metal associated with sulphides and organic matter show very less abundance (Figures 2 - 7). 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 trace metals for organic substances and their decomposition products are of great importance for the release of the metals into water. Trace metal bound to this fraction is assumed to reflect strong association with sediment organic material. The fractionation result from the present study found that affinity of Fe (21.3 - 32.3% of total), Mn (8.6 - 50.6% of total), Cd (0 - 14.6% of total), Cu (14.6 - 38.2% of total), Ni (10.8 - 30.9% of total) and Cr (6.9 - 27.8% of total) were associated with the sulphides and organic (oxidizable) fraction (Figures 2 - 7). On the other hand, after residual fraction major association with this fraction was found with Mn, may be for high affinity with organic matter and also scavenging properties of this fraction. This indicates that Mn occurred in the form of stable organic complexes and metal sulphides. This result is good agreement with the literature reported by Prasad et al. (2006). After amorphous Fe oxyhydroxide phase a major portion of Cu was associated with sulphides and organic matter (Figure 5). Similar tendency of Cu was also reported in several previous studies (Galan et al., 2003; Burton et al., 2005; Prasad et al., 2006). This result is also consistent with the data obtained by the stoichiometric relationship (Table 4). The

Table 4. Stoichiometric relationship between amorphous Fe oxyhydroxide, crystalline Fe oxide, sulphides and organic contents (that is, geochemical fraction abundance), and associated Fe, Mn, Cd, Cu, Ni and Cr as described by linear regression through the origin.

Trace metals	Amorphous Fe oxyhydroxide content		Crystalline Fe oxide fraction		Sulphides and organic fraction	
	Slope	r^2	Slope	r^2	Slope	r^2
Fe	3.25	0.92	3.12	0.77	2.61	0.83
Mn	2.75	0.09	-4.07	0.07	-0.32	0.01
Cu	1.67	0.97	3.82	0.68	3.40	0.38
Ni	2.03	0.81	2.11	0.49	3.60	0.27
Cr	3.38	0.65	1.74	0.72	2.45	0.42

stoichiometric relationships describing trace metals retention by sulphides and organics were 2.61 for Fe, 3.40 for Cu, 3.60 for Ni, 2.45 for Cr and -0.32 for Mn (Table 4) and the affinity order was- Ni > Cu > Fe > Cr > Mn.

Fraction 5 (Silicate and residual fraction)

Metal found in this geochemical phase was in the residual fraction: these are expected to be chemically stable and biologically inactive. The residual or lithogenic fraction is a major carrier of transition metals in most aquatic system. The concentration of trace metals in the crystalline fraction is largely controlled by the mineralogy and extent of weathering trace metals in the form which are not soluble under experimental conditions and hence may be considered to be held within the mineral matrix. In the present study residual form was the dominant form for Mn, Fe and Ni considering each fraction. Fractionation profile of present study indicates affinity of Fe, Mn, Cd, Cu, Ni and Cr were 25.0 - 44.1, 11.8 - 76.7, 1.6 - 18.9, 1.9 - 20.3, 9.8 - 41.8 and 12.6 - 46.9 % of total, respectively for silicate and residual fraction (Figures 2 - 7). The experimental result showed that Cr and Ni mostly occurs (more than 50%) with the first three fractions (AEC, amorphous Fe oxyhydroxide and crystalline Fe oxide phase), though Cr and Ni (12.6-46.9 and 9.8-41.8 % of total, respectively) strongly associated with the residual fraction and this association with inert phase are in agreement with literature data reported by Jain et al. (2008) and Lasheen and Ammar (2009). 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 trace 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).

General geochemical fractionation trend and mobility pattern of trace metal

In this section, a summary of geochemical fractionation results is described and mobility pattern is assessed for a particular trace metal. It is notable from this study results that the proportion of AEC fraction for Cd was relatively high which imply their high risk due to the unstable character of this fraction. Overall, the order of importance of different geochemical fractions of trace metals in Nomi River sediment samples obtained for the study were-

Cd: AEC > amorphous Fe oxyhydroxide > silicates and residual sulphides and organics > crystalline Fe oxide Cu: amorphous Fe oxyhydroxide > sulfides and organics > AEC > crystalline Fe oxide > silicate and residual Cr: silicate and residual > amorphous Fe oxyhydroxide > crystalline Fe oxide sulphide and organics > AEC Ni: silicate and residual > amorphous Fe oxyhydroxide sulphide and organics > crystalline Fe oxide AEC Fe: silicates and residual > sulphide and organics > amorphous Fe oxyhydroxide > crystalline Fe oxide > AEC Mn: silicates and residual > sulphide and organics > amorphous Fe oxyhydroxide crystalline Fe oxide > AEC

These findings suggest that the order of potential trace metals mobility in the aquatic environment of Nomi River is:

Cd > Cu > Cr > Ni > Fe > Mn

Risk assessment code (RAC)

Metals bound to different phases behave differently in the sedimentary and diagenetic environment and therefore have different potentials for remobilization and for the uptake by biota. It is evident from the results of the fractionation study 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 turns assess the risk connected with the presence of metals in an aquatic environment. The risk assessment code (RAC) as proposed by Perin et al. (1985) indicates that sediment which can release in exchangeable and carbonate fraction, less than 1% of the total metal will be considered safe for the environment. On the contrary, 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. The code as applied to the present study reveals that about 39.8 - 89.7% Cd for

Table 5. Assessment of RAC (risk assessment code) in sediment samples collected from the sampling sites of Nomi River, Tokyo, Japan.

Risk assessment code (RAC)	Criteria: Metal (%) in Exchangeable/ carbonate phase	RAC for Nomi River (AEC phase)	
No Risk	<1	-	According to RAC the association of these metal with exchangeable fraction may cause deleterious effect to aquatic life that can be remobilized by changes in environmental conditions such as pH, redox potential, salinity etc.
Low risk	1-10	Fe and Mn	
Medium risk	11-30	Cu, Ni and Cr	
High risk	31-50	-	
Very high risk	>50	Cd	

most of the sites either is adsorb, exchangeable or carbonate bound and therefore comes under the high risk category and can easily enter into the food chain (Table 5). Because of the toxicity and availability of Cd, it can pose serious problem to the ecosystem. Furthermore, according to RAC, Cu, Ni, and Cr (8 - 19.4, 0.6 - 20.1 and 5.6 - 26.5%, respectively were in AEC fraction) are posing medium risk category indicating lower availability, and Fe and Mn having low risk category from which it cannot be easily leached out for the aquatic environment (Table 5).

Enrichment factors (EFc) and trace metal sources

A common approach to estimate the anthropogenic impact on sediments is to calculate a normalized enrichment factor (EFc) for metal concentrations. To evaluate the magnitude of contaminants in the environment, the enrichment factors were computed relative to the abundance of species in source material to that found in the Earth's crust (Huheey, 1983; Atgin et al., 2000). Atgin et al. (2000) reported that crustal enrichment factors (EFc) of elements are frequently used to determine the degree of modification in sediment composition. The following equation was used to calculate the EFc:

$$EFc = (C_M/C_{Al})_{sample}/(C_M/C_{Al})_{Earth's\ crust}$$

Where; $(C_M/C_{Al})_{sample}$ is the ratio of concentration of metal (C_M) to that of Al (C_{Al}) in the sediment sample, and $(C_M/C_{Al})_{Earth's\ crust}$ is the same reference ratio in the Earth's crust. The average abundance of Fe, Mn, Ni, Cd, Cr and Cu (56300, 950, 75, 0.20, 100 and 55 g g^{-1}, respectively) in the reference Earth's crust were taken from Huheey (1983), and Al was selected as the reference element in this study because combination of this element are stable and do not change significantly during the geochemical processes. The reference value of Al is 7.8% (7.5 - 8.1%). However, in Nomi River sediment, highest EFc value was obtained for Cd, were greater than 5 which indicate enrichment of these metals in sediment and for probable explanation, it can be concluded that extensive human and mechanical activities are responsible (Figure. 8). If the EFc value of an element is greater than unity, this indicates that the metal is more abundant in the sample relative to that found in the Earth's crust. Although EFc values less than 5 may not be considered significant, they are indicative of metal accumulation, because such small enrichments may arise from difference in the composition of local sample material with respect to the reference Earth's crust ratio values used in the EFc calculations (Atgin et al., 2000). If the EFc values are greater than 5, samples are considered contaminated. Figure 8 represents the EFc values of all the trace metals measured in the sediment samples of Nomi River and the range were 0.79 - 3.07, 0.47 - 1.85, 1.03 - 4.23, 1.22 - 10.01, 0.43 - 0.74 and 0.26 - 1.34 for Cr, Ni, Cu, Cd, Fe and Mn, respectively. Metallurgical industry in the present study area may be dominating source of anthropogenic Cr emission in to the atmosphere. Another probable contributor for the pollution of this river is Haneda airport, which is very close with the mouth of Nomi River, may be directly or indirectly discharges different metal during washing and cleaning activities of the aircraft. In future, this loading of trace metals in the sediments might increase so as to contaminate the aquatic ecology. Finally, it is presumed that high EFc values in some sites indicate an anthropogenic source of trace metal, mainly from activities such as industrialization, urbanization, deposition of industrial wastes and others as the study area is surrounded by highly industrialized states of Japan.

Comparison of mean value of sum of fraction with background value taken from average shale concentration and Japanese average river sediment data

The average total trace metal concentration in the

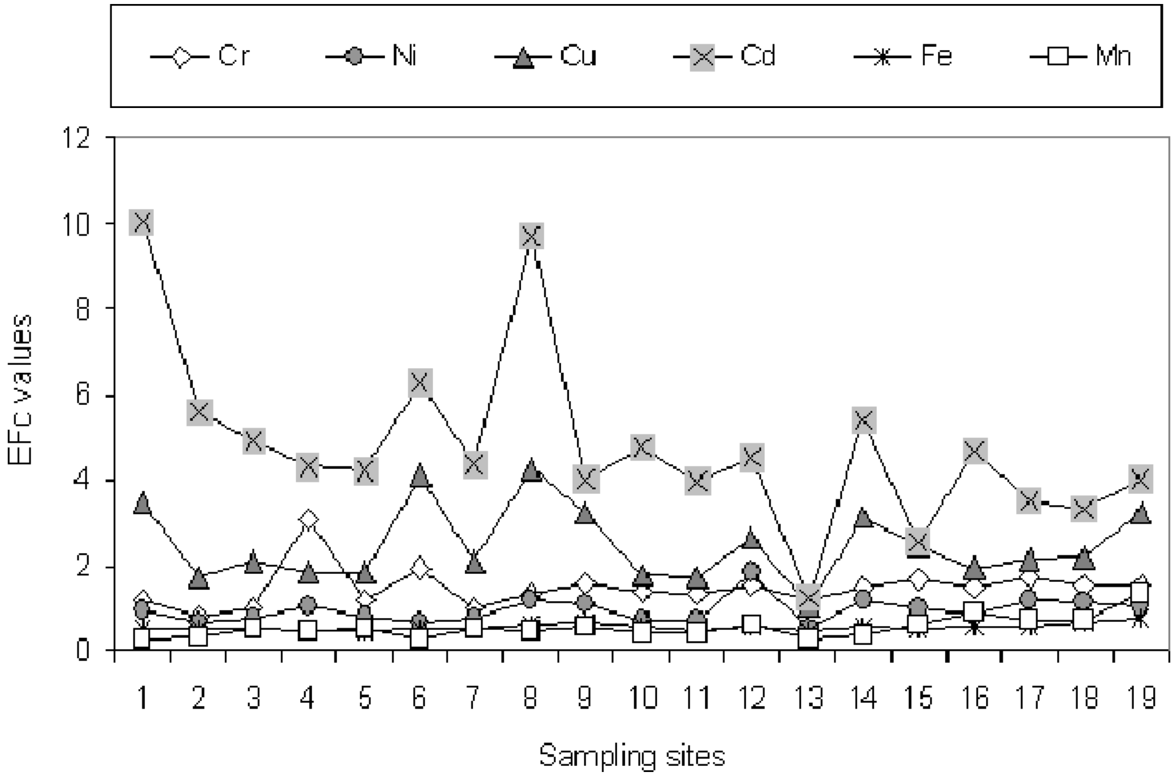

Figure 8. Enrichment factors (EFc) of trace metals in sediment samples at different sampling sites of the Nomi River, Tokyo, Japan.

Table 6. Comparison of mean value of sum of fractions with background value taken from average shale concentration and Japanese average river sediment data.

Trace metals	Mean value of sum of fractions of the present study	Japanese average river sediment value [a]	Average shale value [b]
Fe	26065	61300	47000
Mn	415.58	1260	850
Cd	0.93	0.16	0.3
Cu	125.83	30.6	45
Cr	130.55	65.2	90
Ni	62.2	25.1	68

[a] Gamo, (2007) [b] Turekian and Wedepohl (1961).

sediments of the Nomi River reveals that the concentrations of all the metals (except Fe, Mn and Ni) were higher than the respective average shale value and Japanese average river sediment data (Table 6). The higher values of metal in the river basin may be attributed with couple of sources especially for anthropogenic input from the catchment area, which carry composite waste effluents from different kind of industrial and residential area. In the present study Fe and Mn mean value did not exceed the standard value except sampling site 19, but Ni concentration in some sites exceeded the standard value though the mean value was lower than the standard may be for local enrichment in such site by industrial activity. The result indicates that the levels of trace metals found in the sediments of Nomi River might create an adverse effects on the aquatic ecosystems associated with this river, especially after it receives urban wastes. However the high concentration of Cd, Cu and Cr in most of the sites in Nomi River sediment is very representative to justify the pollution that is originated from human activities.

CONCLUSION

The impact of anthropogenic trace metal pollution and geochemical status on Nomi River sediment was evaluated using EFc and RAC. According to RAC Nomi River possess high risk for Cd, medium risk for Cr, Ni and Cu. The mean total percentage of non-residual phase for Cd, Cu, Cr, Ni and Fe were quite higher than the residual phase which implies higher mobility and availability of these metals and undoubtedly brings about serious environmental harm near future and can be used as fingerprint for the impact of urban activities. Because the non-residual fraction extremely important representing amount of metal that can be easily mobilized by changes in environmental conditions such as pH, redox potential, salinity etc. A large proportion of AEC-bound Cd was found in the Nomi River sediments, which may create a significant pollution load in the surroundings ecosystems. The association of Cu with residual phase was also very low (comprising 8.6%) suggesting higher exposure risk for benthic biota and might have been introduced largely from anthropogenic sources. The order of potential trace metals mobility in the aquatic environment of Nomi River was: Cd > Cu > Cr > Ni > Fe > Mn. Although the average sum of fraction of Fe, Mn and Ni concentration in the sediment is lower than standard value but the bioavailable quantity of these metal is comparatively high and reflect a greater tendency to become bioavailable, which may increase in future if no measures are taken to check the anthropogenic contamination of river water from the catchment. The occurrence of trace metal in Nomi River sediment is due to the discharge of industrial effluent from various sources including untreated sewage, municipal waste, traffic, household garbage from nearby residential areas and others. Hence, speciation study reveals that the role of smaller rivers are very significant which has been ignored over the years and need to be addressed immediately in terms of metal contribution to the world oceans. Finally therefore, there is a need to protect Nomi River from anthropogenic pressure to reduce environmental risk and this study may provide valuable database for future research on Nomi River. Lastly stricter environmental regulation for sediment quality is required to support protection and management strategies for Nomi River ecosystem in Ota Ward of Tokyo, Japan.

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