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Rare Earth Elements and Geochemical Partitioning of Zn and Pb in Sediments of an Urban River

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Abstract: Problem statement: Urban river sediment pollution due to Zn and Pb is a serious problem in all over the world. The source and level of Zn and Pb pollution in sediments of Nomi River of Ota Ward, one of the most industrialized areas in Tokyo, Japan is still lacking. **Approach:** The present study focused on Rare Earth Elements (REEs) and geochemical partitioning of Zn and Pb in sediments of 19 sampling sites of Nomi River in order to examine the mobility pattern. The amounts of Zn and Pb in the liquid extract of 5 (five) geochemical phases were measured by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and the concentrations of REEs in sediments were determined by using X-ray Fluorescence Spectroscopy (XRF). **Results:** Speciation data indicate dominant labile fraction of Zn, which is related to the presence of several anthropogenic influence of the investigated area. Enrichment Factor (EFc) and Index of geoaccumulation (I_{geo}) value were compatible with the result, which confirm pollution status of Zn. Environmental risk of Zn and Pb were also evaluated using the Risk Assessment Code (RAC) and sequential extraction results and found Zn poses high to very high risk (34-59), whereas Pb poses low to medium environmental risk (0-19). **Conclusion:** The mean values of REEs and other minor elements were lower or very close to average shale and Japanese river sediment value but Sr, Sn, Zr and Sb contents were little bit higher than average Japanese river sediment values. Anthropogenic activities, prevalent in the study area play a key role in the accumulation of Zn and Pb in aquatic system. Early warning on the sediment pollution to respective authorities help in preserving the aquatic system from further degradation of the river.

Key words: Rare earth elements, minor elements, geochemical partitioning, sediment pollution, Tokyo

INTRODUCTION

Metallic pollution is a serious problem worldwide due to their toxicity and their ability to accumulate in the biota. One of the most crucial properties of metals, which differentiate them from other toxic pollutants, is that they are not biodegradable in the environment. The concentration of metals in aquatic ecosystems has increased considerably as a result of inputs from human production and consumption activities. In these ecosystems, sediments are the main sink for these elements, but when environmental condition changes (pH, sediment redox potential and others, sediments can act as a source of metals (Forstner, 1989; Izquierdo *et al*., 1997; Zoumis *et al*., 2001). In order to assess the short and long term true environmental impact of pollutants, one of the most important factors to consider is its mobility (Selim and Zhu, 2002). Our earlier investigation showed that chemical composition of Nomi River aquatic sediments has very high total concentrations of several “Urban’’ metals such as Cd, Cr, Cu, Zn, Ni and Pb and most of the samples have exceeded the USEPA’s toxicity reference values for most of those metals (Sharmin *et al*., 2009). The total concentration of metal may be useful as a global index of metal contamination, but it provides inadequate information about bioavailability, toxicity and their impact on the environment (Shrivastava and Banerjee, 2004; Alonso *et al*., 2004). During their transport, the metals undergo numerous changes in their speciation and complexation phenomena (Dassenakis *et al*., 1998; Akcay *et al*., 2003), which affect their behavior and

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bioavailability. Although large rivers constitute major contributors to pollution input into the sea (Ludwig and Probs, 1998; Abril *et al*., 2002), but the impact of small rivers cannot be locally ignored which is the dominant pathway for metals transport (Miller *et al*., 2003). A number of studies on the metal distribution in river sediments and suspended particles and on speciation of metals have been performed (Alonso *et al*., 2004; Chen *et al*., 2005; Nowieriski *et al*., 2006; Zakir *et al*., 2008; Lasheen and Ammar, 2009). Besides, sequential extractions bring in additional data which could help to estimate the fate of metal combinations in different environmental conditions and hence conclude about their bioaccessibility and their toxic effect on environment (Galan *et al*., 2003). It is generally believed that metals in carbonate, sulphide and organic compounds are more toxic due to their higher bioavailability and thus are more critical from an environmental risk assessment standpoint (Karbassi *et al*., 2008). Ota Ward in Tokyo, Japan is considered as one of the most industrialized areas of Japan, hosting almost 5000 especially manufacturing industry such as general machinery, electric machinery and appliance, metal and plastic products, transport and precision machinery and others, which are located along the Nomi River side basin (OCIPA, 2007). The aim of this study was to determine the geochemical partitioning of Zn and Pb in sediments of 19 sampling sites of Nomi River by using a widely used five step sequential extraction procedure (Hall *et al*., 1996). The study also determined the total concentration of REEs and minor elements and measured the pollution levels in sediments due to different anthropogenic activities.

Study area: Ota city is situated in the southeastern part of the Tokyo Metropolis, which is surrounded by several other cities; specially, it faces the Tokyo Bay in the east, Shinagawa and Meguro cities in the north and Setagawa city in the Northwest. The total area is 59.46 km^2 ranking Ota city first among the 23 districts of Tokyo (OCIPA, 2007). The breadth of industries in Ota city is wide and represents a significant industrial zone that supports the whole Japanese industry. Ota city acts as the southern gateway of Tokyo and is an important center for road, rail and air transportation. 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).

MATERIALS AND METHODS

Collection and preparation of sample: Total 19 sediment samples were collected from the whole river by maintaining a distance of about 100 m. Location of the sampling sites is shown in Fig. 1. 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 gm. Sub-samples of the material were dried in an oven at 50°C for 24 h and sieved (aperture 125 μm). 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 sequential extraction analysis was carried out. Extreme care was taken during preparation of sample to avoid external contamination. 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. For the quality control standard and analytical blanks were also prepared and analyzed using the same procedures and reagents.

Determination of REEs and minor elements of sediments: The total concentration of REEs and other minor elements (e.g., V, Br, I, As, Ba, Zr, Rb, Y, Sn, Sb, Cs, La, Ce, Pr and Nd) of sediment samples were determined by X-ray Fluorescence Spectroscopy (XRF) by employing a Rigaku RIX 1000 (Tokyo, Japan) XRF; using powder pellet samples following the manufacturer's recommendations.

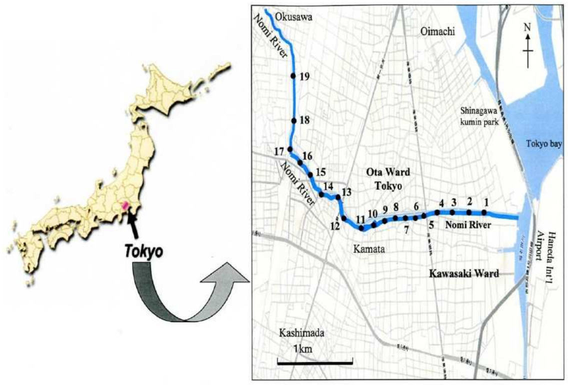

Fig. 1: Locations of the sampling sites of Nomi River in Tokyo, Japan

Sequential extraction experiment: Zinc and Pb speciation in the sediment was done by sequential extraction scheme proposed by Hall *et al.* (1996), which is one of the most thoroughly researched and widely used procedures to evaluate the possible chemical associations of metals in sediments (Zakir and Shikazono, 2008). The amount of Zn and Pb in the extract was measured in the liquid extract by ICP-MS (Hewlett-Packard 4500, USA) at National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan. 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 102 and 94% recovery for Zn and Pb, respectively. Exactly 0.5g sediment sample was weighed and used for the sequential extraction procedure. Each successive extraction was separated by centrifugation at 4000 rpm for 30 min and after then a filtration step was done for ICP-MS determination. All the operations were carried out in 50 mL polypropylene centrifuge tubes (Nalgene, New York) and Teflon (PTFE) containers provided with screw stoppers. As a quality assurance measurement, each sediment sample was subjected to triplicate analyses and the measurements are given as mean, unless noted.

Sediment quality assessment:

Determination of Enrichment Factors (EFc): Enrichment Factorc (EFc) is a useful indicator of reflecting the status of environmental contamination. In order to evaluate the extent of Zn and Pb pollution in Nomi River sediment, the enrichment factors (EFc) were computed relative to the abundance of species in source material to that found in the Earth's crust using the equation proposed by Atgin *et al.* (2000):

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

where, $(C_M/C_{Al})_{sample}$ is the ratio of concentration of heavy 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 Zn and Pb (70 and 12.5 $\mu g\ g^{-1}$, respectively) in the reference Earth's crust were taken from Huheey (1983) and Al (the reference value being 7.8%) was selected as the reference element, due to its crustal dominance and its high immobility. EFc values were interpreted as (Acevedo-Figueroa *et al*., 2006) where EFc<1 indicates no enrichment; 1-3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe and >50 is extremely severe.

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

Determination of geoaccumulation index (I_{geo}): The geoaccumulation index (I_{geo}) values were calculated for Zn and Pb as introduced by Muller (1969) is as follows:

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

Where:

C_n = Measured concentration of metal in the sediment

B_n = 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 (1669), 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), is mainly applies 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

Concentration of REEs and minor elements in sediments of Nomi River: The range and mean of total V, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Th, Se, Br, I and As contents in sediments of Nomi River are presented in Table 2. The mean concentration of Sn and Sb (10.4 and 1.6 µg g^{-1}, respectively), greatly exceeded both the average shale value (Turekian and Wedepohl, 1961) and Japanese river sediment average value (Gamo, 2007), while the average concentration of Sr and Zr (164.3 and 107.8 µg g^{-1}, respectively) and Se, Br and I ((0.99, 34.7 and 3.2 µg g^{-1}, respectively) only exceeded the Japanese river sediment average value (Gamo, 2007) and average shale value (Turekian and Wedepohl, 1961), respectively (Table 2). The mean concentration of other minor elements and REEs were lower than both the average shale value (Turekian and Wedepohl, 1961) and Japanese river sediment average value (Gamo, 2007), which indicate that these elements were originated from lithogenic sources. However, the highest concentration of total V, Zr, Nb, Sn and Ba (171, 161, 9.7, 22 and 463 µg g^{-1}, respectively) were found at site 6, while the maximum concentration of Rb, Cs and Th (90, 4.0 and 10 µg g^{-1}, espectively) were found at site 1 and La, Ce, Pr and Nd (21, 42, 4.0 and 18 µg g^{-1}, respectively) were found at site 13. Moreover, the trend of total Rb, Zr, Nb, Cs, Th, Br and I concentration from Tokyo bay side to the upper side of the river was decreasing which may be due to the effect of mixing of tidal sea water with Nomi River water (Table 2).

Correlation matrix for analyzed REEs and minor elements in sediments of Nomi River was calculated to see if some of the elements were interrelated with each other and the results are presented in Table 3. It will also provide clues about the carrier substances and the chemical association of elements in the study area. The correlation analysis of concentrations data shows weak positive and negative correlations among Pr, Se, Br and I indicating that these elements have complicated geochemical behaviors. On the other hand, good to excellent correlations were observed among V, Rb, Y, Zr, Nb, Sn, Cs, Ba, La and Ce indicating a common source for these elements.

Geochemical partitioning of Zn and Pb in sediments of Nomi River: In the present study, sequential extraction procedure as proposed by Hall *et al.* (1996) has been used to obtain the five fractions (i.e., i) AEC, (ii) Amorphous Fe oxyhydroxide, (iii) Crystalline Fe oxide, (iv) Sulphide and organics and (v) Silicate and residual). These five categories have different behavior with respect to remobilization under changing environmental conditions (Jain *et al.*, 2008).

Table 2: Total concentration (µgg^{-1}) of REEs and minor elements in sediments of Nomi River, Tokyo, Japan analyzed by XRF

Sampling	Concentration (µg g^{-1})																	
site	V	Rb	Sr	Y	Zr	Nb	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Th	Se	Br	I	As
1	148.0	90.0	179.0	17.0	141.0	8.6	21.0	2.30	4.0	412	19.0	39.0	2.0	15.0	10.00	1.00	25.0	0.9	Nd
2	110.0	76.0	170.0	14.0	111.0	6.6	9.0	1.20	3.0	381	17.0	35.0	2.0	13.0	7.00	1.00	15.0	0.7	Nd
3	111.0	67.0	180.0	13.0	99.0	6.0	7.0	1.40	3.0	370	16.0	32.0	2.0	13.0	5.00	1.00	15.0	0.5	Nd
4	93.0	69.0	174.0	13.0	102.0	6.2	7.0	3.40	3.0	380	14.0	28.0	1.0	12.0	4.00	1.00	19.0	2.0	Nd
5	81.0	68.0	157.0	12.0	100.0	5.7	7.0	1.10	2.0	359	16.0	32.0	3.0	13.0	6.00	0.90	61.0	2.0	Nd
6	171.0	78.0	184.0	18.0	161.0	9.7	22.0	3.30	3.0	453	19.0	34.0	1.0	14.0	5.00	1.00	12.0	1.0	Nd
7	93.0	70.0	154.0	13.0	122.0	6.0	6.0	0.80	3.0	376	18.0	33.0	3.0	14.0	6.00	1.00	12.0	1.0	Nd
8	147.0	55.0	164.0	20.0	112.0	8.0	10.0	1.90	3.0	369	17.0	35.0	1.0	13.0	8.00	1.00	24.0	4.0	Nd
9	145.0	57.0	182.0	15.0	108.0	6.3	13.0	2.00	2.0	363	14.0	28.0	2.0	12.0	3.00	1.00	13.0	1.0	Nd
10	123.0	65.0	171.0	15.0	103.0	5.8	7.0	1.00	2.0	370	13.0	29.0	2.0	14.0	4.00	0.90	132.0	14.0	Nd
11	64.0	61.0	169.0	12.0	91.0	5.2	5.0	0.40	2.0	364	15.0	25.0	1.0	12.0	4.00	1.00	57.0	10.0	1.2
12	72.0	53.0	153.0	13.0	87.0	4.9	10.0	0.90	1.0	314	13.0	23.0	3.0	11.0	4.00	1.00	34.0	3.0	Nd
13	124.0	86.0	145.0	19.0	149.0	7.8	5.0	0.50	4.0	375	21.0	42.0	4.0	18.0	7.00	1.00	22.0	3.0	Nd
14	167.0	70.0	200.0	18.0	132.0	7.3	20.0	2.00	3.0	463	17.0	35.0	0.3	14.0	6.00	1.00	24.0	3.0	Nd
15	64.0	52.0	147.0	11.0	78.0	4.2	5.0	1.00	1.0	311	10.0	21.0	2.0	9.0	4.00	1.00	112.0	8.0	Nd
16	68.0	49.0	156.0	11.0	97.0	4.2	6.0	1.00	2.0	302	12.0	25.0	3.0	10.0	3.00	1.00	20.0	3.0	Nd
17	71.0	50.0	150.0	11.0	81.0	4.4	5.0	1.80	2.0	309	12.0	23.0	2.0	10.0	4.00	1.00	43.0	2.0	Nd
18	53.0	46.0	135.0	10.0	82.0	4.3	16.0	1.60	2.0	279	11.0	21.0	0.1	10.0	4.00	1.00	12.0	2.0	Nd
19	92.0	41.0	151.0	12.0	92.0	3.4	16.0	2.00	1.0	286	11.0	24.0	4.0	11.0	3.00	1.00	8.0	0.3	1.1
Mean value	105.1	63.3	164.3	14.1	107.8	6.0	10.4	1.60	2.4	360	15.0	29.7	2.02	12.5	5.10	0.99	34.7	3.2	-
Range	53-167.0	41-90.0	135-200.0	10-20.0	78-161.0	3.4-9.7	5-22.0	0.4-3.40	1.0-4.0	279-463	10-21.0	21-42.0	0.1-4.0	9-18.0	3.00 10.00	0.9-1.00	8.0-132.0	0.3-14.0	Nd-1.20
JRSA*	131.0	69.7	153.0	18.1	56.2	7.5	2.43	0.69	3.9	408	17.2	59.0	4.08	16.4	5.89	-	-	-	9.32
ASV**	130.0	140.0	300.0	26.0	160.0	11.0	6.0	1.50	5.0	580	92.0	59.0	5.6	24.0	12.00	0.60	4.0	2.2	130

Nd = Not detectable; JRSA = Japanese River Sediment Average [29]; ASV= Average Shale Value [27]

Table 3: Correlation coefficient matrix of total concentrations of REEs/minor elements in sediments (n =19) of Nomi River in Tokyo, Japan

	V	Rb	Sr	Y	Zr	Nb	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Th	Se	Br
Rb	0.58																
Sr	0.75	0.47															
Y	0.89	0.61	0.51														
Zr	0.81	0.81	0.49	0.82													
Nb	0.85	0.81	0.60	0.88	0.90												
Sn	0.60	0.19	0.45	0.40	0.49	0.46											
Sb	0.48	0.13	0.47	0.27	0.32	0.41	0.62										
Cs	0.61	0.84	0.41	0.67	0.78	0.80	0.20	0.24									
Ba	0.82	0.80	0.82	0.74	0.81	0.87	0.42	0.37	0.70								
La	0.67	0.88	0.42	0.76	0.88	0.87	0.22	0.07	0.87	0.78							
Ce	0.74	0.87	0.44	0.81	0.86	0.84	0.23	0.10	0.88	0.76	0.94						
Pr	-0.21	0.00	-0.43	-0.12	0.00	-0.27	-0.35	-0.43	-0.16	-0.35	0.03	0.09					
Nd	0.66	0.85	0.36	0.77	0.84	0.77	0.17	-0.02	0.80	0.71	0.90	0.92	0.17				
Th	0.50	0.72	0.22	0.64	0.60	0.70	0.25	0.05	0.76	0.54	0.76	0.82	-0.05	0.66			
Se	0.03	-0.08	0.01	0.06	0.09	0.06	0.20	0.21	0.16	-0.03	0.06	-0.05	-0.15	-0.16	0.02		
Br	-0.22	-0.10	-0.12	-0.17	-0.34	-0.24	-0.39	-0.37	-0.39	-0.12	-0.35	-0.27	0.00	-0.15	-0.17	-0.63	
I	-0.17	-0.12	-0.04	-0.04	-0.26	-0.18	-0.37	-0.42	-0.29	-0.06	-0.27	-0.24	-0.16	-0.06	-0.21	-0.47	0.87

Note: R values >0.40 and >0.54 denotes significant at 5 and 1% level of probability, respectively

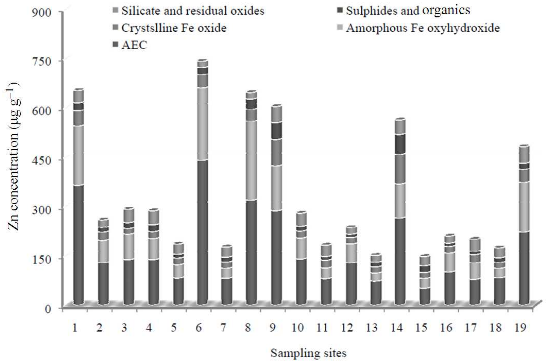

Fig. 2: Geochemical distribution of Zn concentration ($\mu g\ g^{-1}$) in sediments at different sampling sites of Nomi River in Tokyo, Japan

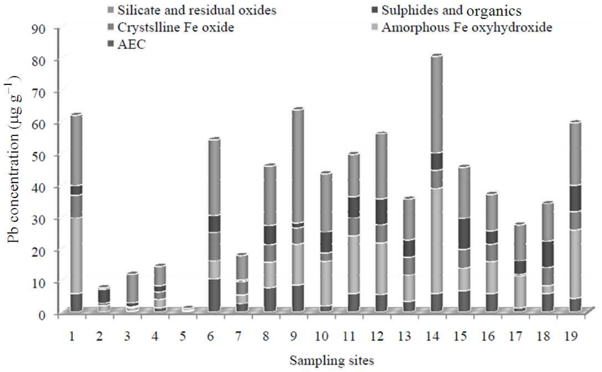

Fig. 3: Geochemical distribution of Pb concentration ($\mu g\ g^{-1}$) in sediments at different sampling sites of Nomi River in Tokyo, Japan

The fractions introduced by human's activity include the adsorptive, exchangeable and bound to carbonates/acid soluble phase, which are considered to be weakly bound metals and may equilibrate with the aqueous phase thus becoming more rapidly bioavailable (Gibbs, 1977). The Fe-Mn oxide/reducible and organic matter/oxidisable phase have scavenging effect and may provide a sink for metals. The release of the metals from the matrix is most likely to be affected by the redox potential and pH. The fractionation pattern of Zn and Pb in Nomi River sediments at different sites are shown in Fig. 2 and 3. With little exception the sum of the extracted fractions do agree with the independently determined total metal concentrations, supporting the overall accumulation of the extraction procedure. We have already reported that the sediments of Nomi River contained higher amount of total Pb and Zn than the standard shale and average Japanese river sediment value and also the waters contained higher amount of Zn (Sharmin *et al*., 2009). But the total Zn and Pb content is not reliable parameter for estimating the toxicity of these metals. And that was not enough to know their environmental association and availability. Therefore, in the present study an attempt has been made to study fractionation profile of Zn and Pb as how much dangerous status are posing and to determine the eco-toxic potential of these metals with main focus both in terms of their toxicity and enrichment strategies. As a consequence, it is necessary to study the Zn and Pb speciation, i.e., their partition into different fractions of the solid materials that form the sediments.

AEC (Adsorbed/Exchangeable/Carbonate) or acid soluble fraction: Preferential association of exchangeable and carbonate bound Zn (34.1-59.3% of total) were found in Nomi River sediments (Fig. 2). This means that there is a significant Zn pollution arriving to this river and may be a threat to the aquatic environment. It is worth mentioning that only the AEC fraction of Zn in sediments of Nomi River exceeded the USEPA's toxicity reference value (110 μg g^{-1}) (US EPA, 1999) except sites 5, 7, 11, 13, 15, 17 and 18. 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). The adsorption of metals is related to changes in water ionic strength that this fraction could be regarded as a pollution indicator (Forstner and Wittmann, 1979). Finally association of Zn with this fraction is probably the best example of human-induced influence in the sediments of Nomi River, which is in good agreement with another river data of Tokyo, Japan (Zakir *et al*., 2008). On the other hand, the AEC fractions recovered for Pb in sediments of Nomi River were comparatively low 0-19.1%, suggesting lower pollution risk (Fig. 3).

Reducible fraction (Amorphous Fe oxyhydroxide and Cryataline Fe oxyhydroxide): The Fe and Mn hydroxide constitutes a significant sink for metals in the aquatic system. This phase accumulates metals from the aqueous system by the mechanism of adsorption and coprecipitation (Bordas and Bourg, 2001). The relatively higher concentrations of elements such as Pb and Zn associated with this fraction are caused by the adsorption of these metals by the Fe-Mn colloids (Purushothaman and Chakrapani, 2007). The geochemical fractionation result from the present study found relatively high affinity of Zn (16.7-37.1% of total) and Pb (0-41.2% of total) for amorphous Fe oxyhydroxide of Nomi River sediments (Fig. 2 and 3). The observed trend in the association of Zn and Pb with amorphous Fe oxyhydroxide as moderately well explained and the presence of Fe oxyhydroxide, such as goethite in the samples of Nomi River was also detected by the XRD which is published in our previous report (Sharmin *et al*., 2010). In contrast to amorphous phases only 5.4-16.0% of total Zn and 0- 3.6% of total Pb were associated with the operationally defined crystalline Fe oxide fraction (Fig. 2 and 3).

Oxidisable fraction (Sulphide and organics): The fractionation result from the present study revealed a comparatively lower affinity of Zn (2.9-13.6% of total) and higher percentage of Pb (0-54.1% of total) with the sulphide and organics fraction (Fig. 2 and 3). This phenomenon for Pb was similar to another result (Svete *et al*., 2001), where authors reported that oxidisable fraction is a significant scavenger of Pb. Lead emissions are mainly from traffic and residential heating (Al-Masri *et al*., 2006) and around 66% of Pb being found to be associated with organic materials and this is due to incomplete burning of vehicles fuel (Al-Masri *et al*., 2006) and a similar trend has also been observed in Nomi River sediment.

Residual fraction (Silicate and residual): In the sequential extraction procedure described in this study, it is necessary to emphasize that a solid residue, mainly made of silicates, remains after the application of all steps. This is insignificant from the geochemical aspect and can be considered as insoluble containing highly immobile metals bound to the silicate matrix. In the present study residual form was dominant for Pb (affinity 8.6-75.0% of total) but very less amount obtained for Zn (affinity 2.7-9.1% of total) (Fig. 2 and 3). The probable explanation for association of Pb in the residual fraction may be due to the incorporation of Pb in alumino-silicate minerals (Yuan *et al*., 2004) therefore, it is unlikely to be released to pore waters through dissociation. So that incorporation into the crystalline structures of minerals particles could be regarded as the major transport mechanism for this metal. The metal present in the residual fraction can be used as a baseline data for the assessment of the degree of the contamination of the system. The stability of this fraction is controlled by the mineralogy and weathering degree of sediment.

General mobility trend: The average percentage of Zn and Pb in each fraction in 19 sampling sites of the study area are listed in Table 4. The experimental results indicate almost half of total Zn content (47.2%) is extracted with AEC fraction, which implies their high risk due to the unstable character of this fraction. On the other hand, the low levels of Pb in non-residual fractions of these sediments indicate toxic effects are unlikely unless significant acidification or accelerated organic matter decomposition takes place. Overall, the order of importance of different geochemical fractions of Zn and Pb in Nomi River sediment samples obtained for the study was- For Zn**:** AEC > amorphous Fe oxyhydroxide > silicate and residual > crystalline Fe oxide > sulphide and organics and for Pb: silicate and residual **>** amorphous Fe oxyhydroxide > sulfides and organics > crystalline Fe oxide > AEC. These findings suggest that the order of potential mobility of Zn and Pb in the aquatic environment of Nomi River is: Zn > Pb.

Table 4: Speciation pattern for Zn and Pb in sediments of Nomi River, Tokyo, Japan and Risk Assessment Code (RAC)

	Average percentage in each fraction (in %)					
Metal	AEC	Amorphous Fe Oxyhydroxide	Crystaline Fe oxide	Sulphide and organics	Silicate and residual oxide	Level of risk on the basis of RAC
Zn	47.2	23.6	12.2	6.7	12.5	High
Pb	9.8	23.0	11.1	13.9	42.0	Low

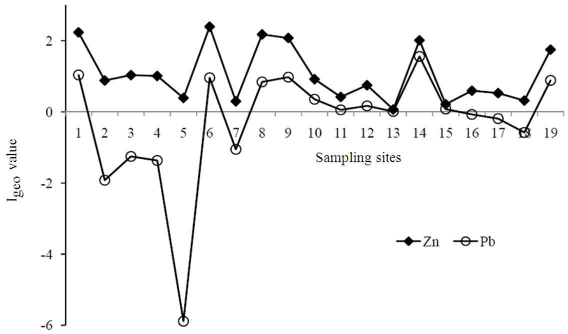

Fig. 4: Geoaccumulation index (Igeo) of Zn and Pb in sediments at different sampling sites of Nomi River in Tokyo, Japan

Risk Assessment Code (RAC): The code as applied to the present study revealed that 34.1-59.3% (average value 47.2) of total Zn of the study 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 1 and 4). Because of the toxicity and availability of Zn it can pose serious problem to the ecosystem and can be remobilized by changes in environmental conditions such as pH, redox potential, salinity and others. On the other hand, only 0-19.1% of total Pb were found in the AEC fraction with an average value of 9.8% are posing no risk to medium risk category indicating lower availability from which Pb cannot be easily leached out for the aquatic environment (Table 1 and 4). So, the potential hazard of Zn is larger than those of Pb which occurred mostly in the inert residual fraction.

Geoaccumulation Index (I_{geo}): The calculated index of geoaccumulation (I_{geo}) of the Zn and Pb in the sediments of Nomi River and their corresponding contamination intensity are shown in Fig. 4. The I_{geo} values for Zn ranged from 0.07-2.4 and corresponded with class 1-3, which exhibited unpolluted to moderately polluted and moderately to strongly polluted sediment quality. The results reveal that Zn contamination of the sediments of Nomi River could have significant impact on aquatic ecology. The I_{geo} values for Pb were negative to 1.4 indicating class 0-2 category, which reflecting unpolluted to moderately polluted sediment by Pb in the study sites.

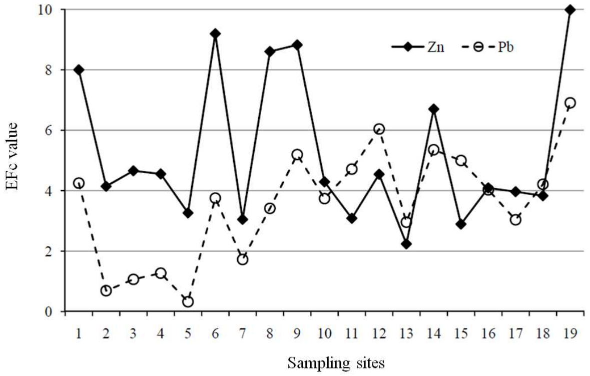

Fig. 5: Enrichment Factors (EFc) of Zn and Pb in sediments at different sampling sites of Nomi River in Tokyo, Japan

Enrichment factors (EFc) and heavy metal sources: Although the high enrichment factor is a first indication of a potential anthropogenic contribution for an element, some natural sources can also cause for the observed enrichment of this chalcophilic elements (Zn and Pb). The calculated EFc values obtained for Nomi River sediment range from 2.2-9.9 for Zn, whereas for Pb the range was 0.02-6.9 (Fig. 5). Among the calculated results, EFc values greater than 5 indicate sediments are contaminated by Zn and Pb, which could be a problem for human and aquatic life. Among the toxic metals present in atmosphere, Zn had been described to be important and tire dust in the urban environment is considered a documented source of Zn as oxide (Adachi and Tainosho, 2004). Indeed, some studies have specified that Zn speciation; especially soluble phases had an important influence on lung injuries (Adamson *et al*., 2000). On the other hand, Pb is identified as more serious public health problem particularly for children. The adverse toxic effect caused by Pb on human is well recognized. Neurological defects, renal tubular dysfunction, anemia are the most characteristics of Pb poisoning (Forstner and Wittmann, 1979). Threats to human health occur when sediment contaminants bioaccumulate in fish and shellfish tissues consumed by humans (Mulligan *et al*., 2001). In future, this loading of heavy metals in the sediments might increase so as to contaminate the standing stock of different kinds of fisheries. Finally, for high EFc values (>2), it is presumed that enrichment corresponding mainly to the anthropogenic input (Hernandez *et al*., 2003), which is concomitant with present findings, as Haneda airport which is located very close to the mouth of the Nomi River, industrialization and heavy traffic are the major contributor for the worst condition of this river.

CONCLUSION

Identification of metal sources and quantitative determination of metals as well as the fate of those metals, are important environmental scientific issues. This study has been focused mainly on geochemical behavior of Zn and Pb in sediment profiles of Nomi River, Tokyo, Japan and presents useful tools and indices for the evaluation of sediment contamination. In the study area Zn is a concern, coming from most probably human induced activities and its main geochemical fraction was AEC, which has much effect on environment and humans, therefore, its input also must be managed meticulously and could be declared as alarming also. Lead is a highly toxic element for aquatic organisms and fish, but its main geochemical fraction was residual and silicate, which has little effect on environment suggesting weak pollution risk. Relationships between metals speciation and total metals concentrations reflected that the order of potential mobility of Zn and Pb in the aquatic environment of Nomi River is: Zn > Pb. According to RAC, Zn poses high to very high risk (34-59), whereas Pb poses low to medium environmental risk (0-19). However, the lower mean percentage of active fractions is an advantage to control the environmental pollution in the Nomi River. Further anthropogenic activities, prevalent in those areas might also play a key role in the accumulation of such metals in aquatic system. Early warning on the river water and sediment pollution to respective authorities help in preserving the aquatic system from further degradation of the river.

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