

## Geochemical Distribution of Trace Metals and Assessment of Anthropogenic Pollution in Sediments of Old Nakagawa River, Tokyo, Japan

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**Abstract:** The geochemical distributions of cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb) and zinc (Zn) were examined in sediments collected from Old Nakagawa River (NR), Tokyo, Japan. A widely used 5-step sequential extraction procedure was employed for the fractionation of the metals and the concentrations were measured in the liquid extracts by inductively coupled plasma mass spectrometry (ICP-MS). The association of Cd (76-98%) and Zn (48-67%) were found highest with AEC (adsorbed/exchangeable/carbonate) phase, Cu (45-60%) and Pb (44-73%) with amorphous Fe oxyhydroxide phase and the maximum fractionation of Cr was in both crystalline Fe oxide (12-60%) and amorphous Fe oxyhydroxide phase (15-60%). For retention by amorphous Fe oxyhydroxide minerals, the observed stoichiometric gradient was: 1.52 for Cu, 1.23 for Pb, 2.25 for Cr and 3.09 for Zn. Corresponding values for association with crystalline oxides and sulphides and organics were an order of magnitude greater than those for amorphous oxyhydroxide, indicating a greater affinity of trace metals for these phases. The total concentration ranges of Cd, Cr, Cu, Pb and Zn in NR sediments were 2.86-16.95, 551.7-3953.1, 340.6-1565.3, 136.9-385.9 and 931.4-3650.1  $\mu\text{g g}^{-1}$ , respectively. The observed order of potential trace metal mobility in the aquatic system was: Cd>Zn>Pb>Cu>Cr. Organic carbon contents in sediment samples were comparatively high (mean 5.48%) and the X-ray diffraction (XRD) study detected the presence of several clay minerals, those are likely to be major host of trace metals in sediments. The sediments of NR was considered to be polluted on the basis of unpolluted sediments and geochemical background values with respect to Cd, Cr, Cu, Pb and Zn. According to the enrichment factors (EF<sub>c</sub>), most of the sites have several times higher values of trace metals than the standard. The study revealed that the pollution in sediments of NR could be linked to anthropogenic activities such as industrialization, urbanization, deposition of industrial wastes and others.

**Key words:** Pollution, anthropogenic effect, trace metals, sediment, fractionation

### INTRODUCTION

Sediments are important carriers of trace metals in the environment and reflect the current quality of the system. With the growing interest in the rules that govern the fate of pollutants in urban environments, the sediments of urban rivers pose a particularly challenging scientific problem. As in natural environments, urban river sediments have a high potential for storage of trace elements. Unlike natural rivers, however, a large proportion of the trace element load contained in urban sediments is not associated with the original geologic parent material, but with the

steady supply of trace elements, both dissolved and in particulate form, carried by treated and untreated urban waters. Thus, a river close to an urban centre has the opportunity to be polluted by both naturally occurring and anthropogenically originated trace 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 Old Nakagawa River (NR) in Tokyo, Japan is a location where a significant amount of different types of

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industrial units were available at the time of second world war<sup>[1]</sup> and the people of that area informed that in some locations a huge amount of industrial metal contained waste was deposited about 30 years ago.

Sediments usually provide a record of catchment inputs into aquatic ecosystems. Natural sediment formed during weathering process might be modified markedly during transportation and deposition by chemicals of anthropogenic origin<sup>[2]</sup>. It is also reported<sup>[3]</sup> about the anthropogenic pollution load of Pb, Cr and Cu in sediments of NR. Excess amount of any metal has toxic effects on plants, animals and human beings. In Japan, there has been variable human damage caused by trace metals, such as copper (Cu) poisoning in the Ashio Cu mine area and the Itai-itai disease induced by cadmium (Cd) in the Kamioka mine area. Therefore, in the Basic Environment Law of Japan<sup>[4]</sup>, there are severe restrictions for Cu and Cd in the environmental standard for the protection of human health.

To assess the environmental impact of contaminated sediments, information on total concentrations is not sufficient and particular interest is the fraction of the total trace metal content that may take part in further biological processes. The overall behaviour of trace metals in an aquatic environment is strongly influenced by the associations of metals with various geochemical phases in sediments<sup>[5,6]</sup>. Sequential extraction techniques have been applied to study the geochemical partitioning of trace metals in contaminated soils<sup>[7,8]</sup> and sediments<sup>[9-13]</sup>. Geochemical distribution results have also been used as an aid in predicting potential contaminant mobility and bioavailability<sup>[14,15]</sup>. It is clear that such information aids our understanding of trace metal behaviour in the environment and is therefore of widespread interest.

The present research aims were, to measure the concentrations of trace metals (Cd, Cr, Cu, Pb and Zn) and their association with various geochemical substrates in sediments of NR, Tokyo, Japan and to assess the contribution of anthropogenic activities in sediment pollution. These results will also be important in reconsidering the existing waste disposal systems and their future impact on natural environment.

**General description of the study area:** Old Nakagawa River 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<sup>[1]</sup>, 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.

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<sup>[16]</sup>. 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<sup>[17]</sup>.

## MATERIALS AND METHODS

**Collection and preparation of samples:** Total 21 sediment samples were collected, among those 17 were from NR, 2 from OR and the other 2 from AR, as described in Fig. 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.

All chemicals and reagents were of analytical reagent grade quality (Sigma-Aldrich, USA and Wako, Japan). Millipore water was used throughout all the experiments. Before use, all glass and plastic ware were soaked in 14% HNO<sub>3</sub> for 24 h. The washing was completed with Millipore water rinse.

**Determination of physicochemical properties of sediments:** The pH was measured in 1:2.5 sediment to water ratio by using a Towa DKK HM-20P pH meter. The suspension was allowed to stand overnight prior to pH determination. The electrical conductivity (EC) was measured in the saturation extract of the sediments, using a Towa DKK CM-21P EC meter. The grain size of the sediments was measured by using a Laser scattering particle size distribution analyzer (Horiba: LA-920, Kyoto, Japan). The carbonate content of the

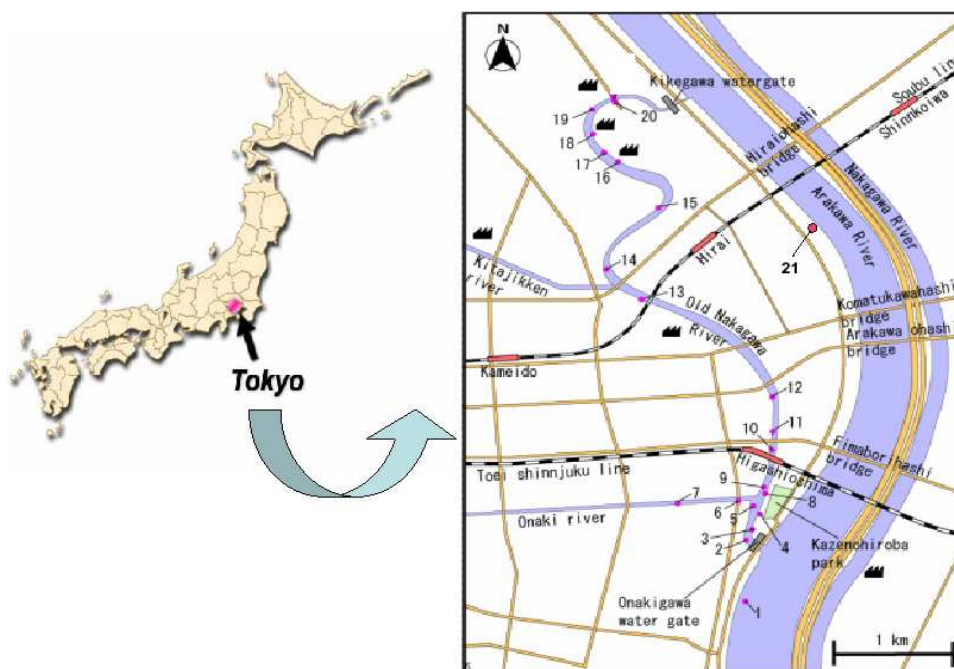


Fig. 1: Locations of the sampling sites in Old Nakagawa, Onaki and Arakawa rivers

sediments was determined by the addition of excess HCl to  $\text{CaCO}_3$ <sup>[18]</sup> and the organic carbon (OC) was measured by the wet oxidation method<sup>[19]</sup>.

**Sequential extraction experiment:** A widely used 5-step sequential extraction procedure<sup>[20]</sup> was employed in this study and the trace metals were measured in the liquid extract by ICP-MS (Hewlett-Packard 4500, USA). During extraction, extractant quality (especially the required pH) maintained carefully. 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. 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 94-102% recovery for the trace metals. 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 measure, each sediment sample was subjected to triplicate analyses and the measurements are given as mean, unless noted.

**Major elemental constituents and mineralogy of sediments:** A preliminary quantitative 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 beads, 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 results calculated considering the loss on ignition and expressed in mass percent. Analytical recoveries for the major elements from JSd-2 ranged 94-108%. A Bruker AXS: D-8 Advance (Berlin, Germany) X-ray diffractometer was employed for XRD analysis.

## RESULTS AND DISCUSSION

**Physico-chemical properties of sediments:** The pH of sediments of the study area ranged from 7.11-8.95 and the mean EC value was 1.22  $\text{S m}^{-1}$  (Table 1). Organic carbon is determined to assess the role played by the organic fraction of sediments in the transport, deposition and retention of trace metals<sup>[18]</sup>. Organic matter in the sediment played an important role in the adsorption of trace metals. Further, it was suggested that the organic matter content in general could be used as a simple pollution index of the sediment<sup>[21,22]</sup>. The

Table 1: Physico-chemical properties of sediment samples of the study area

Sampling sites	pH	EC (S m <sup>-1</sup> )	Organic carbon (%)	Carbonate as % CaCO <sub>3</sub>	Particle size distribution (%)		
					Clay (<2 μm)	Silt (2-50 μm)	Sand (>50 μm)
1	7.64	1.105	3.308	1.69	17.82	46.17	36.01
2	8.11	1.223	4.334	2.55	26.11	48.46	25.43
3	8.15	1.330	4.087	2.10	22.17	47.71	30.12
4	7.68	1.410	5.734	1.73	20.64	42.4	36.96
5	7.37	1.371	5.527	2.10	17.07	43.68	39.25
6	7.55	1.254	5.517	2.18	22.92	39.49	37.59
7	8.95	0.947	4.402	2.00	15.76	37.21	47.03
8	7.34	1.215	4.375	1.63	10.69	29.79	59.52
9	8.18	1.289	5.770	2.58	18.06	39.55	42.39
10	7.80	1.437	6.014	3.51	21.09	42.35	36.56
11	7.43	1.293	5.574	3.44	16.34	31.34	52.32
12	7.55	1.214	5.000	5.34	12.66	34.51	52.83
13	7.82	1.209	8.102	3.86	17.56	41.69	40.75
14	7.99	1.315	6.550	3.48	18.32	35.41	46.27
15	7.79	1.328	8.319	2.61	18.12	40.7	41.18
16	7.57	1.329	7.745	2.78	16.96	35.32	47.72
17	7.84	1.287	8.551	2.51	18.23	43.76	38.01
18	7.78	0.820	3.201	4.19	12.47	27.87	59.66
19	7.98	1.173	5.202	4.35	15.88	41.77	42.35
20	8.55	1.192	5.467	4.09	16.67	38.42	44.91
21	7.11	0.974	2.96	2.03	24.55	43.08	32.37
Range	7.11-8.95	0.82-1.437	2.96-8.551	1.63-5.34	10.69-26.11	27.87-48.46	25.43-59.66
Mean	7.82	1.22	5.48	2.89	18.10	39.56	42.34

organic carbon in the sediment samples was comparatively higher in NR (mean 5.86 wt.%) and OR (mean 4.96 wt.%) than AR (mean 3.13 wt.%) and its content reached the highest values at sampling sites 10, 13, 15, 16 and 17 (6.01, 8.10, 8.32, 7.75 and 8.55 wt.%, respectively). It should be mentioned here, the flow of current in NR and OR is less, which may favors to accumulate high amount of organic matter on the riverbed. Variations of absolute trace metal concentrations reflected variations in textural and/or carbonate and organic matter content<sup>[23]</sup> and trace metal concentrations correlate closely with distributions of mud (<63 μm) and organic carbon<sup>[24,25]</sup>. In present study, a strong positive significant correlation between organic carbon and trace metal concentrations was observed (r values were 0.81, 0.82, 0.80, 0.81 and 0.89 for Pb, Cr, Cu, Cd and Zn, respectively). Carbonate is often an important component of marine sediments and has been found to be an important indicator of provenance and dispersal of terrigenous material<sup>[18]</sup>. Carbonate content in NR sediment varied greatly (range 1.63-5.34% CaCO<sub>3</sub>) with a mean value of 3.1% CaCO<sub>3</sub>. Table 1 also represents the particle size distribution of the sediment samples. According to hydrometer method<sup>[26]</sup>, the sampling sites 8, 12 and 18 had sandy loam-like textures, the site 2 had silty loam-like texture and the others were predominantly loam-like textures. It is stated<sup>[25,27]</sup> that fine loamy, sandy clay loam, clay loam and clay textures had a major influence on the concentrations of Cd, Co, Cr, Cu, Ni and Zn and the

medians were 3-5 fold higher in clayey than in sandy soils. Trace metal concentrations showed a general increase with the increase in clay minerals content and a decrease in the quartz content in the sediments<sup>[6]</sup>. It is also stated that fine silt and clay fractions were good enough to accumulate higher quantities of trace metals in the sediments<sup>[6]</sup>.

**Major elemental composition of the samples:** Major oxide components of sediment samples are listed in Table 2. It is apparent from Table 2 that the oxides of Si, Ti, Al, Mn, Mg, Na and K in sediment samples did not vary greatly among the sampling sites of the study area, but T-Fe<sub>2</sub>O<sub>3</sub>, CaO and P<sub>2</sub>O<sub>5</sub> content varied significantly for NR and OR samples. Major component concentrations suggest, besides the obvious presence of silica, other aluminosilicate minerals, as well as the presence of iron oxides and to a lesser extent, manganese, titanium and phosphorus containing mineral phases.

**Mineralogy of the sediment:** Additional independent information on the component geochemical phases of the sample sites 17 (highly polluted for most of the trace metals studied) and 21 (unpolluted or slightly polluted) was obtained by XRD analysis and the results are presented in Table 3. Quartz has the strongest peak in both the samples, with the relative intensity of 100. The second strongest peak was for feldspar (anorthite) in sampling site 21 (peak intensity, 45.5) and feldspar/

Table 2: Major elemental composition of sediment samples of the study area

Sampling site	Oxides of major element (wt %)									
	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	T-Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
1	60.32	0.88	16.16	8.50	0.10	2.70	2.13	3.08	2.39	0.46
2	57.79	0.84	16.70	9.15	0.13	3.17	2.45	3.43	2.24	0.40
3	56.88	0.83	17.04	9.39	0.11	3.32	2.90	3.38	2.05	0.41
4	57.21	0.78	15.67	10.45	0.11	3.21	2.59	3.68	2.08	0.67
5	56.45	0.81	15.58	9.57	0.12	3.46	2.47	3.74	2.09	0.77
6	57.03	0.83	16.45	10.21	0.10	2.80	2.42	3.67	2.10	0.52
7	61.00	0.79	16.11	8.16	0.10	2.66	3.44	2.95	1.87	0.27
8	60.25	0.73	15.19	9.17	0.11	3.24	3.44	3.25	1.93	0.55
9	56.28	0.80	15.90	9.78	0.12	3.82	3.30	3.46	2.15	0.62
10	55.82	0.80	15.53	9.33	0.10	3.40	3.59	4.27	2.15	0.62
11	55.12	0.73	14.61	11.25	0.12	3.25	3.44	3.83	1.95	0.73
12	54.07	0.69	13.64	8.65	0.11	4.76	5.91	3.60	1.77	0.69
13	54.15	0.78	15.12	8.73	0.09	3.54	4.20	3.94	2.07	0.86
14	55.02	0.72	15.02	9.21	0.10	3.24	4.19	3.97	1.99	0.88
15	53.39	0.82	14.76	9.49	0.08	3.50	3.49	4.32	2.05	0.86
16	53.80	0.75	14.53	10.10	0.08	3.41	3.29	4.57	2.00	1.20
17	53.43	0.76	14.95	9.69	0.11	3.51	3.22	4.55	1.95	0.90
18	60.51	0.68	14.33	7.63	0.10	2.78	5.58	2.75	1.76	0.43
19	54.84	0.70	14.64	8.52	0.11	3.52	5.04	3.36	1.84	0.54
20	57.23	0.78	15.74	9.56	0.12	3.27	3.88	3.44	2.08	0.48
21	62.20	0.89	14.01	7.76	0.09	2.54	2.05	2.94	2.16	0.44

Table 3: Mineralogical constituents of the sample sites 17 (highly polluted for most of trace metals studied), and 21 (unpolluted or slightly polluted)

Minerals	d- value (Å)	Peak intensity (%)	
		Sample ID 17	Sample ID 21
Quartz	3.35	100	100.0
	4.26	33.1	38.5
Feldspar	3.21	27.6	25.9
	4.04	27.4	20.7
	3.75	21.4	18.6
	3.67	17.2	44.3
Feldspar/chlorites	2.82	41.3	-
Anorthite	3.19	29.0	45.5
Micas & illites	9.99	22.4	16.7
Chamosite	7.09	21.8	15.0
Chlorites	3.54	22.7	12.8
	1.54	20.8	17.6
	14.2	20.2	15.6
Biotite/chlorites	4.46	21.1	13.6
	2.46	21.1	12.2
Kaolinite	1.98	29.2	12.1
	2.28	21.4	13.6
Muscovite	2.57	16.2	11.8
Goethite	2.43	21.6	-
Bayerite	2.23	20.2	13.0
Calcite	3.03	21.6	10.5
	1.88	18.1	9.6
Magnetite	2.53	19.2	-

chlorite in sampling site 17 (peak intensity, 41.3), which was absent in site 21. However, quartz, feldspar (such as albite/ anorthite), several clay minerals (such as micas and illites, chamosite, chlorites, kaolinite, biotite and muscovite), bayerite and calcite were common in both sediment samples, although the peak intensity for sampling site 17 was dominant for all clay,

carbonate and hydroxide minerals (Table 3). It is worth mentioning that the presence of iron oxide and hydroxide group minerals, specifically magnetite and goethite were detected in only sampling site 17. The mineral composition of all the samples agrees qualitatively with the major elemental composition determined by XRF (Table 2).

**Geochemical fractionation:**

**AEC (adsorbed/ exchangeable/ carbonate) fraction:**

The extractant used for this fraction was 20 mL of 1M sodium acetate (NaOAc) (pH = 5 adjusted with acetic acid) and then 6 hrs stirring. A large proportion of exchangeable and carbonate-bound Cd (76-98% of total) and Zn (48-67% of total) were found in the NR and OR sediments (Fig. 2 and 6), although there is a report that Zn is commonly found to exist in contaminated soils and sediments mainly in association with Fe and Mn oxides<sup>[28]</sup>. This difference may be due to high pollution load of Zn in NR and OR sediments. Trace metals recovered with the use of 1 M NaOAc adjusted to pH 5 are associated with carbonate minerals. The XRD data listed in Table 3 also indicated the presence of higher amount of carbonate and several clay minerals in NR sediments, which support this finding. However, it has been cautioned<sup>[29]</sup> that trace metals extracted from soils and sediments with 1 M NaOAc adjusted to pH 5 may have also been specifically sorbed to low energy sites on the surfaces of clay minerals, organic matter and oxide minerals, as well as coprecipitated with carbonate minerals. Therefore, it is acknowledged that trace metals associated with this fraction may also be weakly sorbed

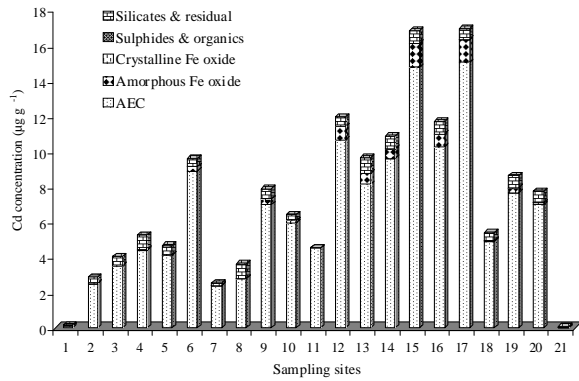


Fig. 2: Geochemical distribution of Cd concentration ( $\mu\text{g g}^{-1}$ ) in sediment samples at different sampling sites of the study area

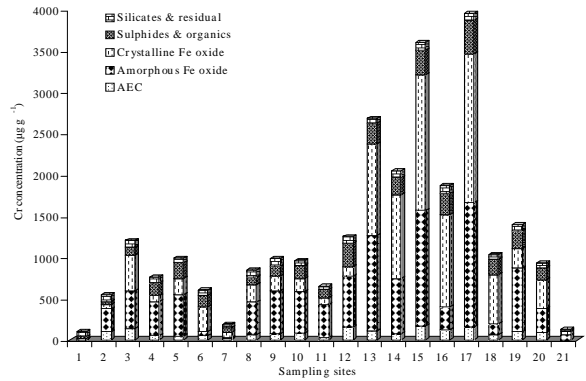


Fig. 4: Geochemical distribution of Cr concentration ( $\mu\text{g g}^{-1}$ ) in sediment samples at different sampling sites of the study area

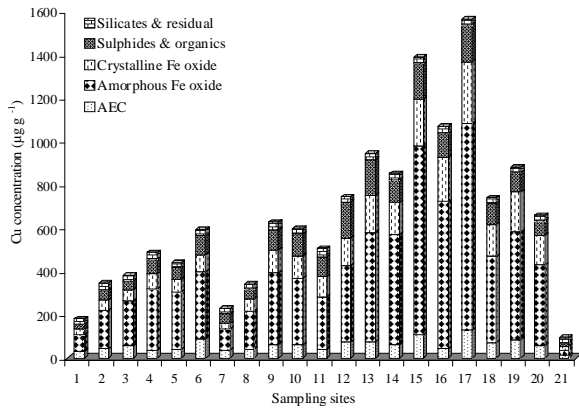


Fig. 3: Geochemical distribution of Cu concentration ( $\mu\text{g g}^{-1}$ ) in sediment samples at different sampling sites of the study area

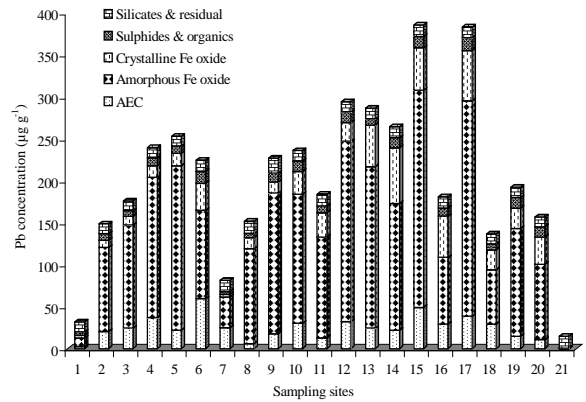


Fig. 5: Geochemical distribution of Pb concentration ( $\mu\text{g g}^{-1}$ ) in sediment samples at different sampling sites of the study area

to other noncarbonate phases. But it is clear that trace metals recovered within this fraction, whether truly associated with carbonates or not, are not strongly bound to the sediment solids and can be released to the sediment pore water in acidic conditions ( $\text{pH} < 5$ ).

Turner and Olsen<sup>[30]</sup> determined extractability of trace metals in contaminated estuarine sediments by chemical and enzymatic extractions. Among the chemical reagents, acetic acid best represented the fraction that was likely to be bioavailable to sediment ingesting biota. Trace metals extractable with 1 M NaOAc adjusted to pH 5 (with acetic acid) are therefore likely to be bioavailable to sediments ingesting and benthic organisms<sup>[31]</sup>. However, the AEC fractions recovered for Cr, Cu and Pb in sediments of NR were comparatively low (3-15, 4-13 and 5-20% of total, respectively) (Fig. 3-5).

**Amorphous Fe oxyhydroxide 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  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 0.25 M HCl and heated for 2 hrs at  $60^\circ\text{C}$ <sup>[20]</sup>. Oxyhydroxide minerals, along with organic matter, have long been recognized as the predominant trace metal sorbents in aquatic systems. In comparison with carbonate minerals, amorphous oxyhydroxide minerals have relatively large surface area and surface site density<sup>[5,32,33]</sup>.

The geochemical fractionation results from the present study found relatively high affinity of Cr (15-60% of total), Cu (45-60% of total), Pb (44-73% of total) and Zn (25-43% of total) for amorphous Fe oxyhydroxide minerals of NR and OR sediments (Fig. 3-6). The observed trends in the association of Cr, Cu, Pb and Zn with amorphous Fe oxyhydroxide

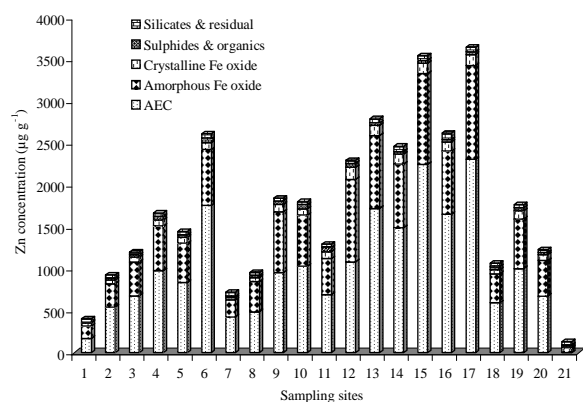


Fig. 6: Geochemical distribution of Zn concentration ( $\mu\text{g g}^{-1}$ ) in sediment samples at different sampling sites of the study area

minerals were moderately well explained and the presence of Fe oxyhydroxide minerals, such as goethite in the samples of NR also detected by the XRD (Table 3). The linear regression (through the origin) parameters for stoichiometric relationships are presented in Table 4, which provides information about the explanation of the observed fractionation trends. In particular, the slope of the regression lines represents the stoichiometry of Cr, Cu, Pb and Zn interaction with the amorphous Fe oxyhydroxide fractions. This relationship provides a quantitative indication of the affinity of a given metal for a particular geochemical fraction<sup>[34]</sup>. For retention by the amorphous Fe oxyhydroxide minerals, the observed stoichiometric gradient was: 2.25 for Cr, 1.52 for Cu, 1.23 for Pb and 3.09 for Zn (Table 4). In terms of the stoichiometric affinity of different trace metals for amorphous Fe oxyhydroxide, the affinity order was:

$$\text{Zn} > \text{Cr} > \text{Cu} > \text{Pb}$$

**Crystalline Fe oxide fraction:** The extractant used for this fraction was 30 mL of 1 M  $\text{NH}_2\text{OH.HCl}$  in 25% acetic acid (HOAc) and then the content was heated at 90°C for 3 hrs. In contrast to amorphous Fe oxyhydroxide minerals, there was no association of Cd with this fraction (Fig. 2). On the other hand, only 10-20% of total Cu, 2-6% of total Zn and 3-27% of total Pb were associated with the operationally defined crystalline Fe oxide fraction (Fig. 3, 5 and 6). This probably reflects the much greater surface area of amorphous minerals in comparison with crystalline material<sup>[35]</sup>. On the other hand, the association of Cr in this fraction (12-60% of total) was almost similar to the amorphous Fe oxyhydroxide phase. The presence of Fe

oxide minerals (such as magnetite; peak intensity 19.2) in NR sediments also supported by the XRD data presented in Table 3. For retention by crystalline Fe oxide minerals, the observed stoichiometric gradient was: 1.76 for Cr, 4.98 for Cu, 2.74 for Pb and 22.72 for Zn and the values were in general greater than for amorphous minerals except for Cr (Table 4). These data indicate that crystalline oxide minerals have a much greater stoichiometric affinity for Cu, Pb and Zn than do amorphous oxyhydroxide minerals. However, in terms of the stoichiometric affinity of different trace metals for crystalline Fe oxide, the affinity order was:

$$\text{Zn} > \text{Cu} > \text{Pb} > \text{Cr}$$

Trace metals associated with oxide (both amorphous and crystalline) minerals are likely to be released in reducing condition. Reductive dissolution of the oxide minerals occurs at Eh less than approximately +250 mV for Mn oxides and +100 mV for Fe oxides<sup>[36]</sup>. Relatively small changes in Eh toward reducing conditions would cause reduction of Fe and Mn oxide species<sup>[34]</sup>. This will cause dissolution of Fe and Mn oxide minerals, thereby allowing release of associated Cr, Cu, Pb and Zn.

**Sulphides and organics fraction:** Trace metals bound to this fraction is assumed to reflect strong association with sediment organic material. Similar to crystalline Fe oxide fraction, there was no association of Cd and only 6-25% of total Cr, 10-22% of total Cu, 0.5-3% of total Zn and 2-9% of total Pb were associated with the operationally defined sulphides and organics fraction (Fig. 2-6). As with the oxide mineral fractions, the trends in association with the sulphides and organics fraction were explained by the stoichiometric relationship data presented in Table 4. The stoichiometric relationships describing trace metals retention by sulphides and organics were 9.38 for Cr, 6.71 for Cu, 16.87 for Pb and 20.11 for Zn and the affinity order was:

$$\text{Zn} > \text{Pb} > \text{Cr} > \text{Cu}$$

Although this result is not consistent with the tendency of Cu to be associated with the sulphides and organics (oxidizable) fraction has been reported in several previous studies<sup>[9,28,34,37]</sup>. This difference may be due to a significant contribution of anthropogenic inputs in NR and OR sediments.

**Silicates and residual fraction:** In the sequential extraction, trace metals in the silicates and residual fraction are notably fixed within the crystalline lattice

Table 4: Stoichiometric relationship between amorphous Fe oxyhydroxide content, crystalline Fe oxide content, and sulphides and organic contents (i.e., geochemical fraction abundance), and associated Cr, Cu, Pb and Zn as described by linear regression through the origin

Trace metals	Amorphous Fe oxyhydroxide-bound		Crystalline Fe oxide-bound		Sulphides and organics-bound	
	Slope	r <sup>2</sup>	Slope	r <sup>2</sup>	Slope	r <sup>2</sup>
Cr	2.25	0.84	1.76	0.90	9.38	0.74
Cu	1.52	0.98	4.98	0.94	6.71	0.71
Pb	1.23	0.91	2.74	0.41	16.87	0.48
Zn	3.09	0.91	22.72	0.75	20.11	0.06

Table 5: Comparative analysis with geochemical background and toxicological reference values for river sediments (units in µg g<sup>-1</sup>)

Trace metal	Geochemical background		US DOE <sup>c</sup>			Canadian EQG <sup>d</sup>			Ontario MOE <sup>f</sup>		Japan MOE <sup>g</sup>	This study (average)	
	Shale standard <sup>b</sup>	Continental crust <sup>b</sup>	TEC	PEC	HNEC	ISQG	PEL	US EPA <sup>e</sup> TRV	LEL	SEL	EQS	UP/SP sediment	Old nakagawa river sediment
Cd	0.30	0.10	0.59	11.7	41.1	0.60	3.5	0.60	0.60	10	1.0	0.12	8.2
Cr	90	100.00	56.00	159.0	312.0	37.30	90.0	26.00	26.00	110	0.01 (Cr <sup>6+</sup> )*	117.10	1511.5
Cu	45	55.00	28.00	77.7	54.8	35.70	197.0	16.00	16.00	110	125.00	137.70	740.0
Pb	20	12.5-20	34.20	396.0	68.7	35.00	91.3	31.00	31.00	250	0.01*	23.50	229.5
Zn	95	70.00	159.00	1532.0	541.0	123.00	315.0	110.00	120.00	820	-	269.60	1918.3

TEC = Threshold effect concentration; PEC = Probable effect concentration; HNEC = High no effect concentration; ISQG = Interim sediment quality guideline; PEL = Probable effect level; TRV = Toxicity reference value; LEL = Lowest effect level; SEL = Severe effect level; UP/SP = Unpolluted/ slightly polluted; EQS = Environmental quality standard and \* means in solution

<sup>a</sup>: Turekian and Wedepohl (1961)<sup>[40]</sup>

<sup>b</sup>: Taylor (1964)<sup>[41]</sup>

<sup>c</sup>: Jones *et al.* (1997)<sup>[42]</sup>

<sup>d</sup>: CEQG (Canadian Environmental Quality Guidelines)<sup>[43]</sup>

<sup>e</sup>: US EPA (U. S. Environmental Protection Agency)<sup>[44]</sup>

<sup>f</sup>: OMOE (Ontario Ministry of Environment)<sup>[45]</sup>

<sup>g</sup>: MOE<sup>[4]</sup>

and are usually considered to be fragments of the primary mineral phase. All other fractions can be of secondary mineral phases as they involve materials formed through physical and chemical processes of weathering of primary minerals. The concentrations of trace metals in the primary phase mainly depend on the weathering degree and process of the primary minerals in sediments, which may create regional variations in the chemical partitioning of trace metals. As it was mentioned earlier, AR has high current flow and the water level is about 3 meter high compare to NR and OR, which facilitate the primary minerals of AR sediment to go with more physical and chemical weathering. However, this fraction is not available to biological or diagenetic processes except over very long time scales<sup>[38]</sup>.

In the present study, trace metal concentration ranges for this fraction were 0.16-0.89, 39.2-95.7, 24.4-36.0, 11.6-17.9 and 30.6-77.2 µg g<sup>-1</sup> for Cd, Cr, Cu, Pb and Zn, respectively for NR sediments (Fig 2-6). The association between trace metals and the residual fraction of uncontaminated soils is so strong that metal association with nonresidual fractions has been used as an indicator of anthropogenic enrichment<sup>[39]</sup>.

**General geochemical fractionation trends:** In this section, a summary of geochemical fractionation results

is described for a particular trace metal. Overall, the order of importance of different geochemical fractions of trace metals in NR and OR sediment samples obtained for the study were:

- Cd: AEC>>silicates and residual>amorphous Fe oxyhydroxide
- Cr: Crystalline Fe oxide≈amorphous Fe oxyhydroxide>silicates and residual and organics>AEC>silicates and residual
- Cu: Amorphous Fe oxyhydroxide>>crystalline Fe oxide>silicates and residual and organics>AEC>silicates and residual
- Pb: Amorphous Fe oxyhydroxide>>crystalline Fe oxide>AEC>silicates and residual and organics>silicates and residual
- Zn: AEC>>amorphous Fe oxyhydroxide>crystalline Fe oxide>silicates and residual and organics≈silicates and residual

These findings suggest that the order of potential trace metal mobility in the aquatic environment of NR is:

$$Cd > Zn > Pb > Cu > Cr$$

**Comparative analysis with background and toxicological reference values:** The available data for a



comparative analysis with background and toxicological reference values for river sediments are summarized in Table 5, along with average values obtained for trace metals of NR and AR sediments. It is evident from Table 5 that average total concentration of all studied trace metals for NR sediments exceeded the geochemical background (shale standard and continental crust)<sup>[40,41]</sup>, but the average concentration of Cd, Cr and Pb for AR sediments are very close to geochemical standard values although the Cu and Zn concentrations were almost three fold higher. However, when compared with effect-based toxicological levels the situation was also quite alarming for NR sediments. The mean total concentrations of all trace metals determined for NR were higher than Ministry Of Environment (MOE), Japan's Environmental Quality Standard<sup>[4]</sup>, US Department of Energy's (US DOE)<sup>[42]</sup> Threshold Effect Concentrations, Canadian Environmental Quality Guidelines (Canadian EQG)<sup>[43]</sup>, US Environmental Protection Agency's (US EPA) Toxicity Reference Values<sup>[44]</sup> and Ontario Ministry of Environment's (Ontario MOE) Lowest Effect Levels<sup>[45]</sup>. It is also evident from Table 5 that the Probable Effect Concentrations and High No Effect Concentrations defined by the US DOE for Cr, Cu and Zn were surpassed by the mean total concentrations of these same elements in the sediments of NR<sup>[42]</sup>. Lastly, all the trace metals (except Cd and Pb) total mean concentrations also exceeded the Severe Effect Level defined by the Ontario MOE<sup>[45]</sup>. The results indicate that the levels of trace metals found in the sediments of NR might create an adverse effects on the aquatic ecosystems associated with this river, especially after it receives urban water and waste waters.

**Enrichment factors (EFc):** One widely used approach to characterize degree of anthropogenic pollution is to establish enrichment ratios. 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<sup>[46-48]</sup>. Crustal enrichment factors (EFc) of elements are frequently used to determine the degree of modification in sediment composition<sup>[48]</sup>. The following equation was used to calculate the EFc:

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

where,  $(C_M/C_{Al})_{\text{sample}}$  is the ratio of concentration of trace metal ( $C_M$ ) to that of Al ( $C_{Al}$ ) in the sediment sample and  $(C_M/C_{Al})_{\text{Earth's crust}}$  is the same reference ratio in the Earth's crust. The average abundance of Cd, Cr, Cu, Pb and Zn (0.20, 100, 55, 12.5 and 70  $\mu\text{g g}^{-1}$ ,

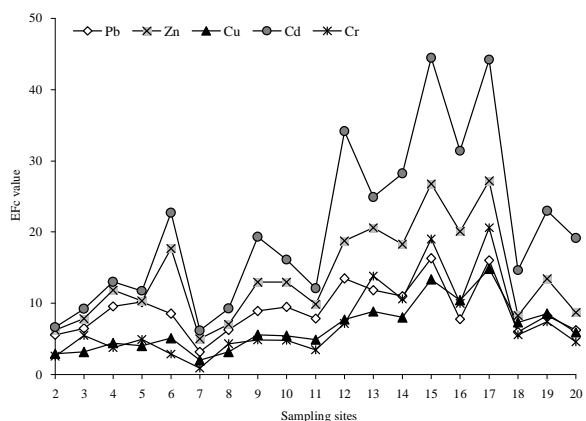


Fig. 7: Enrichment factors (EFc) of trace metals in sediment samples at different sampling sites of the study area

respectively) in the reference Earth's crust were taken from Huheey<sup>[46]</sup> and Al was selected as the reference element, due to its crustal dominance and its high immobility. Furthermore, XRF data for this study (Table 2) also indicate consistency for this element. The reference value of Al is 7.8% (7.5-8.1%).

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 differences in the composition of local sample material with respect to the reference Earth's crust ratio values used in the EFc calculations<sup>[48]</sup>. If the EFc values are greater than 5, samples are considered contaminated. Figure 7 shows the EFc values of all the trace metals measured in the sediment samples of NR and OR. It is evident from the Fig. 7 that all the sampling sites of NR, have EFc values between 5-50 for Cd, Zn and Pb. On the other hand, only 6 sampling sites (2-5, 8 and 11) for Cu and 7 sampling sites (2, 4, 8-11 and 20) for Cr have no significant enrichment values (<5.0). In case of OR sediment, sampling site 6 has enrichment >5 for all the trace metals except Cr and site 7 has significant enrichment only for Cd and Zn. It is presumed that high EFc values indicate an anthropogenic source of trace metals, mainly from activities such as industrialization, urbanization, deposition of industrial wastes and others. Since, the bioavailability and toxicity of any trace metals in sediments depends upon the chemical form and concentration of the metals<sup>[49]</sup>, it can be inferred that trace metals in sediment samples with the highest EFc values, along with higher labile fractions in

sediments have a potential for mobility and bioavailability on the aquatic ecosystems.

### CONCLUSION

A detailed examination on geochemical fractionation, comparison with previous research on river sediments, toxicological reference values and backgrounds indicate that Cd, Zn and Pb and to a lesser extent Cu and Cr are anthropogenically enriched in NR sediments. Concentrations of the trace metals were so high that toxicological effects can be expected in the aquatic ecosystems associated with NR. A large proportion of exchangeable and carbonate-bound Cd ( $2.5\text{-}15.0\text{ mg g}^{-1}$ ) and Zn ( $490\text{-}2310\text{ mg g}^{-1}$ ) were found in the NR sediments. The association of Cu, Cr, Pb and Zn with the operationally defined amorphous Fe oxyhydroxide, crystalline Fe oxide and sulphides and organics fractions were linearly dependent on the abundance of each respective geochemical phase.

This study provides valuable information on the potential mobility of trace metals in river sediments polluted by the anthropogenic influences such as industrialization, urbanization, deposition of industrial wastes and others. Geochemical partitioning results suggest that the order of potential trace metal mobility in NR aquatic environment, is:  $\text{Cd} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cr}$ . If the magnitude of trace metal pollution in the river system increases continuously and this may have severe impacts on the aquatic organisms in the river. It is therefore recommended that in order to check this trend, the industrial establishments and the municipal council or the Government of Japan should reconsider the existing waste treatment and disposal systems and or introduce more efficient one for urban sediments.

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