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Distribution of Metals in Surface Sediments from a Small River Flowing Through Urban and Agricultural Areas

Yuri Igari · Takaaki Tamura · Masaki Ohno · Kazuyuki Suzuki · Tomohiro Kose · Kuniaki Kawata

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Abstract The characteristic distributions of 12 metals (Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd and Pb) were investigated in surface sediments from a small river (Niitsu River) flowing through both urban and agricultural areas by comparison with those from the upper main stream (Nodai River). Among the investigated metals, the mean concentrations of Al, Cr, Fe, Zn, Cd and Pb in the Niitsu River were significantly higher than those in the Nodai River. The investigated sites can be characterized by the principal components 1–3.

Keywords Surface sediment · Metal · River · Principal component analysis · Cluster analysis

In fluvial environments, sediments are the fundamental components serving as the sink of a range of metals. Metals in river sediments are produced from various natural (Woitke et al. 2003) and anthropogenic sources. As anthropogenic sources of metals, traffic (Birmili et al. 2006; Haus et al. 2007; Lough et al. 2005) and petroleum (Amoli et al. 2006) have been reported. The metals derived from these anthropogenic sources were provided to the sediments through direct atmospheric deposition, and through municipal, residential and industrial discharges (Demirak et al. 2006).

Although numerous studies of the distributions of metals in sediments from large rivers such as the Mississippi River (Balogh et al. 2009), the river Danube (Woitke et al. 2003), and the Yellow River (Liu et al. 2009) have been performed, few reports in the literature describe the distribution in sediments from small rivers (Komai et al. 2005). The Nodai River, a tributary of the Shinano River, flows 33.4 km through agricultural areas in Niigata Prefecture, Japan. The Niitsu River is a small branch (5.6 km long) of the Nodai River, which again joins the Nodai River (Fig. 1). The Niitsu River flows through both urban and agricultural areas. Residential, municipal and industrial discharges as well as agricultural drainage flow into the river. Moreover, oil fields were located in the drainage basin of the river, producing some crude oil there until 1996. Therefore, small amounts of oil issue from the bank and the bottom of the Niitsu River around sites five and six (Fig. 1). Some of the oil extracted from the ground flows into site 15 through a residential drainage.

The objective of this study was to assess the recent distribution of the common metals in the surface sediments from the Niitsu River for their potential sources by comparison with those from the Nodai River. The target metals were Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd and Pb.

Materials and Methods

Sediment samples were collected at 18 sites from the Niitsu River and at five sites from the Nodai River (Fig. 1) during October–November 2008. The sediment samples were dried at 105°C for 8 h in an oven; then sieved (2 mm grain size). The obtained sediments were mixed well and stored at 5°C in the dark.

The target metals in sediment samples were determined according to the official method used for bottom sediment

Y. Igari · T. Tamura · M. Ohno · T. Kose · K. Kawata (✉)
Faculty of Applied Life Sciences, Niigata University of Pharmacy and Applied Life Sciences, 265-1 Higashijima Akiha-ku, Niigata, Niigata 956-8603, Japan
e-mail: kawata@nupals.ac.jp

K. Suzuki
Center for Environmental Science in Saitama, 914 Kamitanadare, Kazo, Saitama 347-0115, Japan

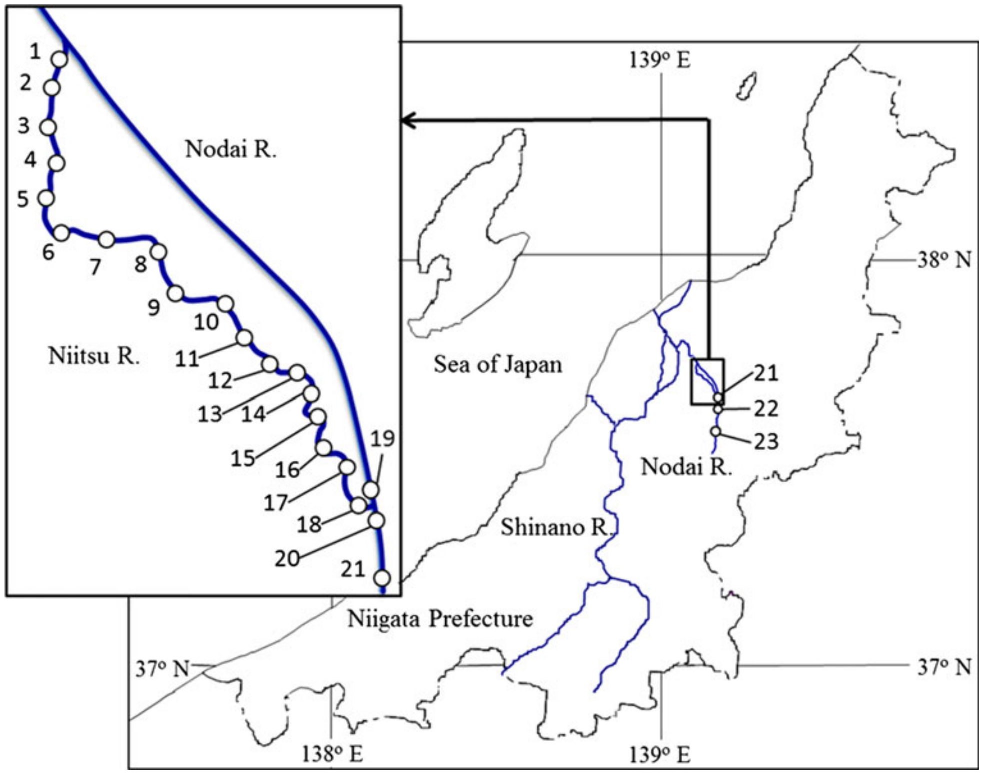

Fig. 1 Sampling sites

surveys (Ministry of Environment 2001). In brief, 0.5 g of a dried sediment sample was digested with 10 mL HNO_3 (69 %–71 %, Ultrapur-100; Kanto Chemical Co. Inc.) and 10 mL HCl (35 %–37 %, Ultrapur-100; Kanto Chemical Co. Inc.). The resulting solution was determined using ICP-MS (SPQ 9000; SII Nano Technology Inc.) with In and Bi as internal standards. The ICP-MS conditions were the following: radio frequency power 1.1 kW, plasma gas flow 16 L/min, nebulizer gas flow 0.98 L/min, auxiliary gas flow 1.1 L/min. The quantification ions (m/z) were 27 for Al, 48 for Ti, 52 for Cr, 55 for Mn, 56 for Fe, 59 for Co, 58 for Ni, 63 for Cu, 64 for Zn, 88 for Sr, 114 for Cd, 208 for Pb, 115 for In and 209 for Bi. A soil standard reference material (SRM 2586; National Institute of Standards and Technology) was determined to evaluate the accuracy and the precision of the method. The recoveries and the relative standard deviations of the target metals from the reference material ranged from 61 % (Cr) to 97 % (Cd) and 1.3 % (Mn) to 12 % (Fe), respectively. The minimum determination limits were 0.6 mg/kg for Al, 4 mg/kg for Fe, 1 mg/kg for Cu and 0.2 mg/kg for the other metals. The organic content (OC) was estimated as the loss upon ignition (550°C, 15 h) and calculated as the percent dry weight (Emilsson and Rolf 2005).

A software package, STATISTICA 06 J (StatSoft Japan Inc.) was used for principal component analysis (PCA) and cluster analysis. Each of the metal concentrations was standardized to a mean of 0 and standard deviation of 1 for the cluster analysis. Ward's Method, which minimizes the mean square distance between the center of a cluster and each member, was used as the algorithm of the cluster analysis.

Results and Discussion

The metal concentrations in the sediment are summarized in Table 1. Among the target metals, the Al concentration found in this study was comparable to those of 18,700–50,200 mg/kg in the sediments from the Danube River system (Woitke et al. 2003) and 17,000–85,000 mg/kg from the Keelung River, Taiwan (Huang and Lin 2003) except for sites 19 and 20. The Cr concentration found in this study was higher than that of 6.26–65.6 mg/kg from the rivers in Hyogo prefecture, Japan (Komai et al. 2005), and lower than those of 14–900 mg/kg from the rivers in Kawasaki City, Japan (Hayashi et al. 2005) and 26.5–556.5 mg/kg from the Danube River system (Woitke et al. 2003). The Mn concentration in this study was comparable to those of 170–1,000 mg/kg from the rivers in Japan and Taiwan (Hayashi et al. 2005; Huang and Lin 2003; Komai et al. 2005). The Fe concentration in this study was almost comparable to those of 21,000–29,500 mg/kg from rivers in Suzhou City, China (Mei et al. 2011), 17,000–56,000 mg/kg from the Keelung River (Huang and Lin 2003), 17,600–64,600 mg/kg from the Danube River system (Woitke et al. 2003) and 16,000–65,000 mg/kg

Table 1 Metal concentrations in river sediments

Site	Concentration (mg/kg dry)												OC (%)
	Al	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sr	Cd	Pb	
Niitsu river													
1	24,000	370	21	440	52,000	11	200	43	300	22	0.5	33	6.9
2	30,000	500	54	880	130,000	16	560	92	860	19	1.3	50	11
3	34,000	330	44	830	100,000	14	420	108	560	23	1.5	45	14
4	16,000	280	15	330	45,000	7.6	190	44	180	13	0.4	22	5.0
5	34,000	230	32	690	70,000	14	310	110	430	27	1.7	48	14
6	26,000	450	36	560	74,000	10	260	68	270	14	1.2	33	17
7	13,000	200	15	200	16,000	4.3	120	30	210	12	0.5	18	3.3
8	33,000	300	29	460	120,000	9.1	250	72	390	21	1.2	45	13
9	13,000	380	12	210	15,000	4.5	99	17	130	10	0.2	14	1.7
10	25,000	260	41	440	47,000	18	280	67	280	25	1.3	41	10
11	19,000	250	31	390	34,000	13	190	52	220	21	<0.2	45	7.9
12	63,000	1,600	210	450	60,000	52	350	61	200	23	<0.2	25	11
13	22,000	600	31	480	29,000	25	170	31	160	67	<0.2	20	5.6
14	23,000	310	19	360	27,000	8.5	160	55	230	19	0.5	43	11
15	27,000	440	61	440	39,000	32	240	58	250	42	0.3	40	9.2
16	26,000	570	32	550	42,000	12	250	48	180	18	0.9	33	7.2
17	25,000	330	10	490	34,000	10	200	53	200	23	<0.2	56	8.4
18	21,000	710	16	330	26,000	6.4	150	12	85	20	<0.2	26	2.1
Mean	26,000	450	39	470	53,000	15	240	57	290	23	0.7	35	10
Max	63,000	1,600	210	880	130,000	52	560	110	860	67	1.7	56	17
Min	13,000	200	10	200	15,000	4.3	99	12	85	10	<0.2	14	1.7
Nodai river													
19	8,400	1,100	10	400	21,000	10	320	20	91	16	<0.2	4.5	0.75
20	10,000	870	15	440	30,000	15	340	150	130	16	<0.2	8.1	1.8
21	15,000	1,100	20	500	24,000	15	400	150	140	23	<0.2	11	2.0
22	17,000	600	14	490	33,000	12	290	130	100	19	<0.2	7.9	1.5
23	13,000	700	20	710	30,000	22	450	240	130	16	<0.2	16	3.4
Mean	13,000	870	16	510	28,000	15	360	140	120	18	<0.2	10	1.9
Max	17,000	1,100	20	710	33,000	22	450	240	140	23	<0.2	16	3.4
Min	8,400	600	10	400	21,000	10	290	20	91	16	<0.2	4.5	0.75
Total													
Mean	23,000	540	34	480	48,000	15	270	74	250	22	0.5	30	7.3
Max	63,000	1,600	210	880	130,000	52	560	240	860	67	1.7	56	17
Min	8,400	200	10	200	15,000	4.3	99	12	85	10	<0.2	4.5	0.75

from rivers in Japan (Komai et al. 2005; Hayashi et al. 2005) except for sites 2, 3 and 8. The Cu and Zn concentration levels found in this study were respectively comparable to those of 54–1,040 and 41–173 mg/kg in Suzho (Mei et al. 2011). The maximum concentrations of Cu and Zn found in this study were lower than those of 700 and 5,400 mg/kg, respectively, in Yokohama (Hayashi et al. 2005). The Cd concentration in the Niitsu River was comparable to those of 0.10–1.56 mg/kg from rivers in Hyogo (Komai et al. 2005) and 0.34–1.11 mg/kg from the Ciliwung River, Indonesia (Yasuda et al. 2011), whereas the Cd concentration in the Nodai River was lower than those in the other rivers. The Pb concentration found in this study was lower than those of 5.1–950 mg/kg in Yokohama (Hayashi et al. 2005), 8.83–198 mg/kg in Hyogo (Komai et al. 2005), 14.7–542 mg/kg from the Danube and 9.3–200 mg/kg from the Keelung River (Huang and Lin 2003).

The differences in the means of the metal concentrations between the Niitsu River and the Nodai River were evaluated using *t* tests. No statistically significant difference was found in the means of Mn, Co, Cu and Sr between the

Table 2 Factor loadings, eigenvalues and contribution rates of PCs

Metal	Factor loading			
	PC1	PC2	PC3	PC4
Al	0.709	−0.382	−0.506	0.189
Ti	−0.022	−0.890	0.214	0.202
Cr	0.493	−0.723	−0.376	0.260
Mn	0.830	0.033	0.423	−0.240
Fe	0.890	0.241	−0.020	0.143
Co	0.391	−0.849	−0.209	−0.165
Ni	0.681	−0.268	0.644	0.014
Cu	0.292	−0.194	0.800	−0.186
Zn	0.857	0.366	−0.005	0.024
Sr	0.128	−0.260	−0.379	−0.851
Cd	0.715	0.529	−0.062	0.105
Pb	0.626	0.444	−0.443	−0.100
Eigenvalue	4.58	3.03	2.06	1.03
Contribution rate (%)	38.2	25.2	17.2	8.6

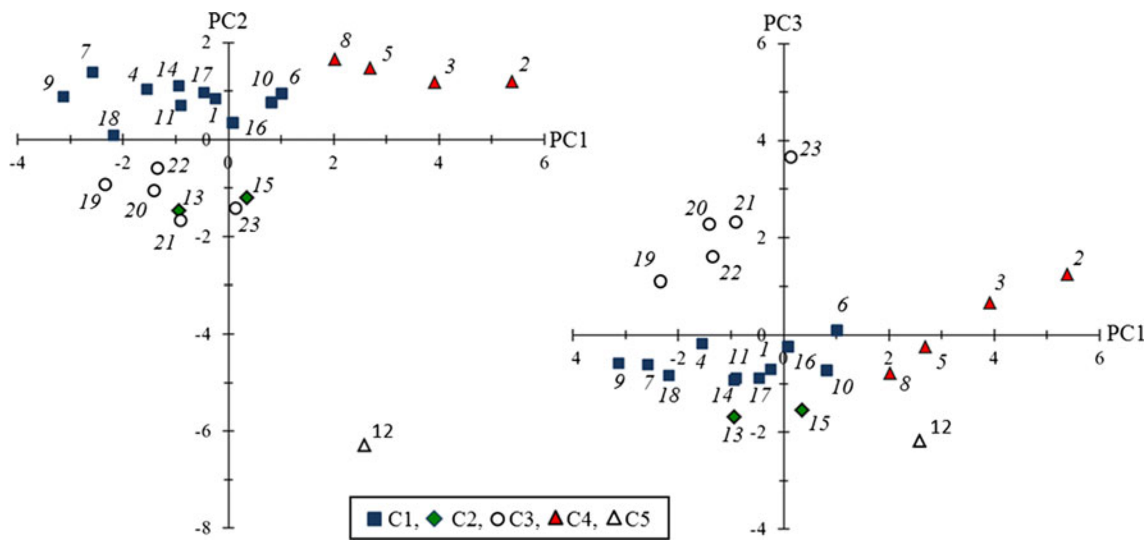

Fig. 2 Score plots of PC2 versus PC1 and PC3 versus PC1. The *italic figures* show the numbers of the investigated sites

two rivers. Results show that these elements were not derived from local sources in the Niitsu River Basin. However, the mean concentrations of Ti and Ni in the Niitsu River were significantly lower than those in the Nodai River. In contrast, the mean concentrations of Al, Cr, Fe, Zn and Pb in the Niitsu River were significantly higher than those in the Nodai River. Moreover, the Cd concentration in the Niitsu River was apparently higher than that in the Nodai River, where Cd was not detected at every investigated site. Among the investigated metals, Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb were reported as traffic-related metals (Birmili et al. 2006; Haus et al. 2007; Lough et al. 2005). Ti, Mn, Fe, Ni, Cu, Zn, Sr and Pb were also derived from petroleum to related materials (Amoli et al. 2006; Datangel and Goldfarb 2011). Therefore, Al, Cr, Fe, Zn, Cd and Pb to the Niitsu River might be derived primarily from these extra anthropogenic sources.

High concentrations of Mn, Fe, Ni, Cu, Zn and Pb were observed mostly downstream (sites 2 and 3) with a few exceptions found in the upper stream. Because the sites are located at a major traffic bridge, they were affected by road traffic. However, the concentrations of Al, Ti, Cr and Co were the highest in the concentrations at the midstream site 12, which is located downstream of an agricultural drainage outlet. These metals were derived primarily from that drainage. High concentrations of the metals were observed at site 5 (Mn, Cu, Zn and Pb) and site 6 (Mn) located in areas of oil production at the bank and the bottom of the

Niitsu River. Site 15, where the concentrations of Cr, Co and Sr were high, was affected by oil-bearing drainage from the previous oil field, which suggests that some of these metals were derived from the oil. In addition, OC in the Niitsu River was significantly higher than that in the Nodai River, suggesting the inflow of organic compounds from the Niitsu River Basin including municipal, residential, and industrial discharges.

The datasets of the metal concentrations in sediment at sites 1–23 were analyzed using PCA. The first five principal components (PC1–PC5) respectively explained 8.2 %, 25.2 %, 17.2 %, 8.6 % and 4.1 %, of the contribution rate in the original data. Therefore, the principal components PC1–PC4 were selected because the results did not significantly change when PC5 was considered. The four principal components explained 89.2 % of the total variance. Table 2 shows the factor loadings for the metals, the eigenvalues, and the contribution rates of the principal components PC1–PC4. PC1 showed a significant correlation with the concentrations of Mn, Fe, and Zn having factor loading values more than 0.81. PC1 also correlated with Al, Ni and Cd (factor loadings greater than 0.64) as well as Cr and Pb (factor loadings greater than 0.49). Moreover, the PC1 scores correlated significantly ($r = 0.928$) with the sum of the metal concentrations ($p < 0.01$). Consequently, PC1 substantially described the general loading of the sediment with the main metals. PC2 showed significant negative correlations with the concentrations of Ti, Co and Cr having factor loading values <-0.64 as well as a positive correlation with the Cd concentration. Consequently, the sites with low PC2 scores were more influenced positively by Ti, Co and Cr, and more negatively by Cd. PC3 responded positively with concentrations of Ni and Cu, and was also characterized by the negative effect of Al. In PC4, the Sr concentration showed a significant absolute loading (>0.81).

The similarities in the distribution patterns of the metals from the investigated sites were assessed using cluster analysis. Sites 1–23 were divided into five clusters at the distance of seven. Although cluster 3 (C3) definitely included the five sites (sites 19–23) in the Nodai River, the other clusters included sites in the Niitsu River. Clusters 2, 4 and 5 (C2, C4 and C5) included two sites (sites 13 and 15), four sites (sites 2, 3, 5 and 8) and one site (site 12), respectively; cluster 1 (C1) included the other 11 sites in the Niitsu River. Although C5 was a unique cluster with the highest Al, Ti, Cr, and Co concentrations of the investigated sites, the other clusters showed no apparent shared characteristics. However, the investigated sites from the two rivers were characterized by PC1, PC2 and PC3. The PCA score plots of PC2 versus PC1 and PC3 versus PC1 are presented in Fig. 2. That is, C1, C2 and C3 included the sites with scores of PC1 <1.5; the PC2 scores were more than 0 in C1, and <0 in C2 and C3, whereas the PC3 scores were −0.1 to 0.2 in C1, <−1.5 in C2, and more than 1.0 in C3. In contrast, C4 and C5 included sites with PC1 scores that exceeded 1.5; the sites in C4 had higher PC2 and PC3 scores than the site in C5. Consequently, the investigated sites were divisible into five clusters, which can be characterized by the scores of PC1, PC2 and PC3.

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