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Chemical Speciation of Metals in Surface Sediments from Small Urban and Agricultural Rivers

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Abstract Characteristic distributions of Al, Mn, Fe, Ni, Zn, and Pb were investigated in the surface sediments of a small river (Niitsu River) flowing through both urban and agricultural areas, along with comparison with those from the upper main stream (Nodai River). The mean compositions of the most mobile metals were ordered as Zn = Mn > Ni = Pb = Fe > Al in the Niitsu River. They were Mn = Zn = Pb = Fe > Ni = Al in the Nodai River. Mn, Fe, Ni, and Zn in the Niitsu River showed higher compositions of mobile (2.9 %–36 %) and oxidizable (6.6 %–16 %) phases than those in the Nodai River. The Ni and Zn in the Niitsu River also had higher reducible phase composition (15 % and 16 %, respectively). In the Niitsu River, Pb had the higher oxidizable composition (29 %). Over 90 % of Al was in the lithogenic phase in the two rivers.

Keywords Metal · Sequential extraction · Surface sediment · River · Fractionation · Mobility

Metals in aquatic environments are derived from various natural and anthropogenic sources. Most metals entering aquatic environments are associated with fine-grained particulates, resulting in their accumulation in bottom sediments (Farkas et al. 2007). Therefore, the assessment of metals in sediments is an important component of the quality assessment of aquatic environments (Yu et al. 2011). The metals are distributed in sediment as different chemical forms associated with organic and inorganic phases, depending on chemical and geological conditions. The chemical speciation of the metals using their partitioning patterns is extremely important for the potential bioavailability and mobility of these metals in the sediments (Farkas et al. 2007; Morillo et al. 2004).

Although several studies have been performed to assess chemical speciation of the metals in sediments from large rivers (Farkas et al. 2007; Hu et al. 2009), few have presented the speciation in sediments from small rivers. We previously investigated the recent metal distribution in surface sediments from the Niitsu River for their potential sources by comparison with those from the Nodai River (Igari et al. 2012), a tributary of the Shinano River flowing 33.4 km through agricultural areas in Niigata Prefecture, Japan. The Niitsu River is a small 5.6-km-long branch of the Nodai River, flowing through both urban and agricultural areas as well as a small oil producing area, subsequently joining the Nodai River again. Municipal, industrial and agricultural drainage as well as small amounts of oil flow into the Niitsu River. The study objective was to assess the forms in which metals are associated with surface sediments from the Niitsu River for their potential bioavailability and mobility of these metals by comparison with those from the Nodai River. The target metals were Al, Mn, Fe, Ni, Zn, and Pb.

Several sequential extraction methods were evaluated for the chemical speciation of the different chemical forms of metals (Dollar et al. 2001; Perez–Santana et al. 2007). Among the methods, the BCR (European Community Bureau of Reference) sequential extraction procedure is a widely used one that reportedly provides the best approximation of the chemical forms (Perez–Santana et al. 2007).

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This method was applied to sediments from rivers (Farkas et al. 2007; Hu et al. 2009) and a freshwater canal (Yu et al. 2011). Therefore, we selected the BCR method for the chemical speciation of metals in this study.

Materials and Methods

Sediment samples were collected at 18 sites (sites 1–18) from the Niitsu River and five sites (sites 19–23) from the Nodai River during October–November 2008 (Igari et al. 2012). The sediment samples were dried at 105°C for 8 h in an oven, and then sieved (grain size 2 mm). The obtained sediments were mixed well and stored at 5°C in the dark. Reagents were purchased from Kanto Chemical (Tokyo, Japan).

Sequential extraction of the metals was performed according to the optimized BCR protocol (Larner et al. 2007; Perez–Santana et al. 2007). The target metals in a sediment sample were extracted sequentially into four fractions, the acid extractable fraction (exchangeable, carbonates; F1), the reducible fraction (iron/manganese oxides; F2), the oxidizable fraction (sulfides, organics; F3) and the residual fraction (lithogenic; F4). The fourth fraction was calculated by subtracting the sum of the first three extractable fractions from the total metal contents (Igari et al. 2012). In brief, 0.5 g of a dried sediment sample was shaken with 20 mL of 0.11 M acetic acid for 16 h at 22 ± 2°C at 400 rpm. The extract was separated from the solid phase by centrifugation at 3,000×*g* for 20 min (F1). To the solid residue was added 20 mL of 0.50 M hydroxylammonium chloride solution adjusted to pH 1.5 with 2.0 M HNO_3. The mixture was shaken for 16 h at 22 ± 2°C at 400 rpm; then the extract was separated from the solid phase by centrifugation at 3,000×*g* for 20 min (F2). Then 5 mL of 8.8 M H_2O_2 (pH 2) was added carefully in small aliquots to the residue obtained in the previous step, and digested at room temperature for 1 h with occasional manual shaking. The mixture was then heated at 85 ± 2°C for 1 h and the volume reduced to a few milliliters by further heating. To the residue was added 5 mL of 8.8 M H_2O_2 (pH 2) and heated at 85 ± 2°C for 1 hour. Then, 25 ml of 1.0 M ammonium acetate solution (pH 2) was added to the residue and shaken for 16 h at 22 ± 2°C at 400 rpm. The extract was separated from the solid phase by centrifugation at 3,000×*g* for 20 min (F3). The three obtained extractable fractions were digested according to the official method for bottom sediment survey (Ministry of Environment 2001). The metal amounts were determined using ICP–MS with In and Bi as internal standards (Igari et al. 2012).

Results and Discussion

The metal concentrations on the dry basis in each fraction are summarized in Table 1. Yu et al. (2011) reported the Zn

Table 1 Metal concentrations in each fraction

	Al concentration (mg/kg)				Mn concentration (mg/kg)				Fe concentration (mg/kg)			
	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4
Niitsu River (sites 1–18)												
Mean	270	500	1,590	24,000	176	41	53	204	1,370	6,300	3,200	42,500
Max	1,640	1,020	2,560	59,200	362	92	173	504	2,940	12,000	7,010	114,800
Min	87	200	520	11,500	33	<0.2	5.1	94	250	210	190	11,000
Nodai River (sites 19–23)												
Mean	61	290	440	11,900	76	26	14	390	230	3,400	470	23,700
Max	73	440	670	15,900	109	68	17	534	290	10,600	1,020	30,400
Min	47	210	340	7,800	9.9	4.1	7.2	330	130	480	40	18,800

	Ni concentration (mg/kg)				Zn concentration (mg/kg)				Pb concentration (mg/kg)			
	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4
Niitsu River (sites 1–18)												
Mean	15	35	29	165	107	41	47	90	1.2	1.2	10	23
Max	62	74	91	345	315	93	116	339	11	5.9	20	56
Min	1.9	8.2	<0.2	83	19	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	3.4
Nodai River (sites 19–23)												
Mean	1.2	11	<0.2	346	12	6.8	6.4	90	0.4	2.8	<0.2	6.2
Max	2.3	21	<0.2	422	19	12	8.9	118	0.7	4.6	<0.2	11
Min	<0.2	2.6	<0.2	280	7.4	2.9	<0.2	68	<0.2	1.8	<0.2	2.5

and Pb concentrations in F1–F4 in surface sediments from the south sections of the Grand Canal of China. Zn ranged in concentrations 112–754 mg/kg in F1, 26.4–125 mg/kg in F2, 15.9–66.9 mg/kg in F3 and 27.4–418.6 mg/kg in F4. The Pb concentrations were 8.2–25.0 in F1 mg/kg, 18.9 –80.4 mg/kg in F2, 2.1–16.4 mg/kg in F3 and 4.5–30.4 mg/kg in F4. The Zn concentrations in F2–F4 and Pb concentrations in F3–F4 in the Niitsu River were comparable to those in the Grand Canal, whereas Zn in F1 and Pb in F1–F2 in the Niitsu River as well as all the metals in the Nodai River were lower than the corresponding concentrations in the Grand Canal. It is suggested that F3 of the BCR scheme corresponds to binding of metals by sulfides and organics (Larner et al. 2007). In this study, however, no consistent trend was found for oxidizable metals with the organic content (Igari et al. 2012).

The metal compositions in F1–F4 in river sediments at sites 1–23 are presented in Fig. 1. Among the investigated metals, F1 and F3 compositions of Ni showed increased tendencies toward the downstream sites. Accordingly, F4 composition of Ni showed a decrease tendency. Moreover, the F1 composition of Zn showed an increased tendency toward the downstream sites. Among the investigated sites, site 14 in the Niitsu River showed characteristic compositions in five metals. Namely, the compositions of Al (7.2 %), Fe (7.8 %) and Pb (25 %) in F1 were the highest among the investigated sites, whereas those of Mn (89 %, which was the same as that at site 19 in the Nodai River) and Zn (85 %) in F4 were the highest. Site 14 is located downstream of a residential drainage outlet that contains oil extracted from the ground (Igari et al. 2012). Therefore, the drainage can affect characteristic compositions.

The mean compositions of the metals in the two rivers are shown in Fig. 2. Among the investigated metals, the mean compositions of Mn and Zn in F1 in the Niitsu River (35 % and 36 %, respectively) were the highest. They were significantly higher than those in the Nodai River (15 % and 11 %), as described later. It is assumed that F1 contains weakly bound metals, which can be mobilized easily into the aquatic phase (Morillo et al. 2004). Therefore, Mn and

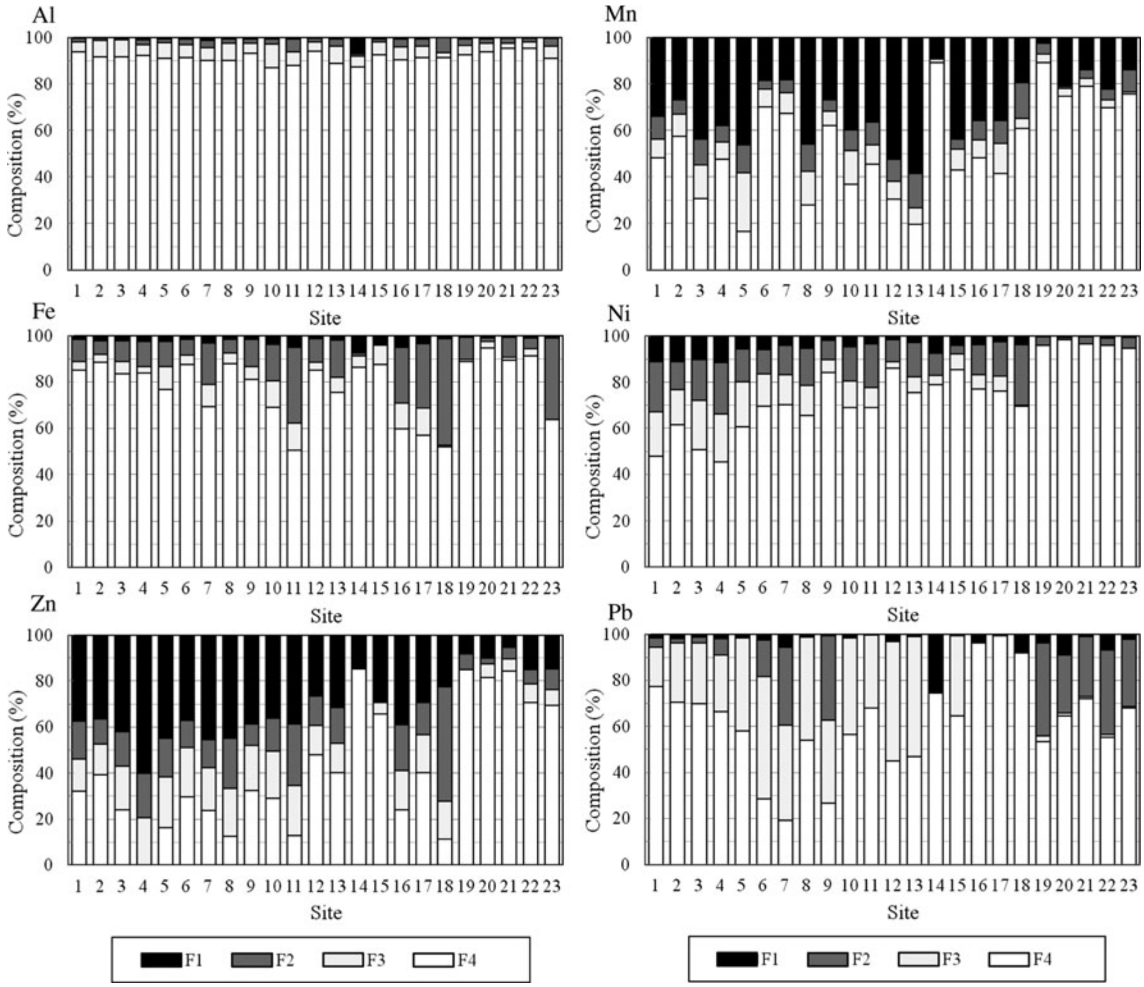

Fig. 1 Metal compositions in fractions in the river sediments

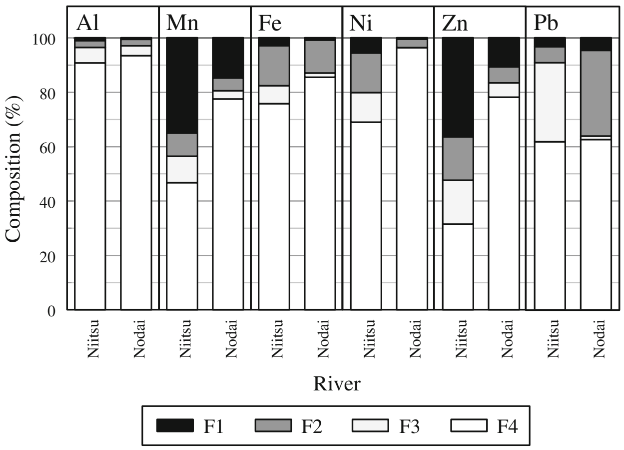

Fig. 2 Mean metal compositions in the two rivers

Zn in the Niitsu River had the highest potential mobility in the investigation. In addition, F4 compositions of Mn (47 %) and Zn (32 %) in the Niitsu River were lower than those in the Nodai River and the other metals. The mean F2 compositions of Fe in the two rivers as well as those of Ni and Zn in the Niitsu River were high (12 %–16 %). Particularly, the F2 composition of Pb (31 %) in the Nodai River was the highest in the F2 compositions in this investigation. The ratios of the reducible metals were high in these cases. However, the mean F3 composition of Pb in the Niitsu River was the highest (29 %) in the investigation with subsequent F3 of Zn (16 %), Ni (11 %) and Mn (9.7 %) in the Niitsu River. Al had the highest compositions in F4; the mean compositions were 91 % in the Niitsu River and 93 % in the Nodai River. The ratios were comparable to the F4 composition (96 %) of Ni in the Nodai River. Results show that Al in the two rivers and Ni in the Nodai River had the highest natural origin (Morillo et al. 2004) and the lowest mobility among the investigated metals.

The differences in the means of the metal concentrations and compositions in each fraction between the Niitsu River and the Nodai River were evaluated using the *t* test. The results are presented in Table 2. According to the differences in means of the metal compositions in F1 (the most mobile and bioavailable composition), the metals can be ranked as $Zn = Mn > Ni = Pb = Fe > Al$ in the Niitsu River. They are $Mn = Zn = Pb = Fe > Ni = Al$ in the Nodai River. The orders in the two rivers differed from the reported order ($Zn > Mn > Ni > Pb > Fe$) in marine sediments from the southwest coast of Spain (Morillo et al. 2004).

The mean of total Al concentration (26,400 mg/kg) in the Niitsu River was significantly higher than that (12,700 mg/kg) in the Nodai River (Igari et al. 2012). The mean Al concentrations in all the fractions in the Niitsu River were also significantly higher than those in the Nodai River. Regarding the composition, no statistically significant difference was found in the Al compositions in F1 and F2 between the two rivers. However, the mean Al composition in F3 in the Niitsu River was significantly higher than that in the Nodai River. Table 1 shows that the mean Al concentrations in F3 were 1,590 mg/kg in the Niitsu River and 440 mg/kg in the Nodai River. Therefore, the excess (1,150 mg/kg) of the mean concentration of Al in F3 in the Niitsu River to that in the Nodai River accounted for 8.4 % of the excess (13,700 mg/kg) of the total Al concentration in the Niitsu River. Furthermore, the mean Al composition in F4 in the Niitsu River (91 %) was significantly lower than that in the Nodai River (93 %). However, the mean compositions were regarded as almost identical, and the excess (12,100 mg/kg) of Al in F4 in the Niitsu River was calculated as 88 % of that in all Al concentration.

The mean concentration (176 mg/kg) and composition (35 %) of Mn in F1 in the Niitsu River were significantly higher than those (76 mg/kg and 15 %) in the Nodai River, respectively. Furthermore, the mean concentration (53 mg/kg) and composition (9.7 %) of Mn in F3 in the Niitsu River were significantly higher than those (14 mg/kg and 3.0 %) in the Nodai River, respectively. The mean excess concentrations in F1 and F3 in the Niitsu River were 100 and 39 mg/kg, respectively. However, the mean

Table 2 Differences in means of metal concentrations and compositions in two rivers

	Concentration			Composition		
	$M_{NI}^{a} > M_{NO}^{b}$	$M_{NI} < M_{NO}$	–[c]	$M_{NI} > M_{NO}$	$M_{NI} < M_{NO}$	–
F1	Al*, Mn**, Fe**, Ni**, Zn**		Pb	Mn**, Fe**, Ni**, Zn**		Al, Pb
F2	Al**, Ni**, Zn**		Mn, Fe, Pb	Ni**, Zn*	Pb**	Al, Mn, Fe
F3	Al**, Mn**, Fe**, Ni**, Zn**, Pb**			Al*, Mn**, Fe**, Ni**, Zn**, Pb**		
F4	Al**, Fe**, Pb**	Mn**, Ni**	Zn		Al*, Mn**, Ni**, Zn**	Fe, Zn, Pb

[a] Mean in Niitsu River, [b] Mean in Nodai River, [c] No significant difference

** Significant difference ($p < 0.01$); * Significant difference ($p < 0.05$)

concentration (204 mg/kg) and composition (47 %) of Mn in F4 in the Niitsu River were significantly lower than those (390 mg/kg and 78 %) in the Nodai River, respectively. The sum excess of the mean Mn concentration (139 mg/kg) in F1 and F3 in the Niitsu River was comparable to the decrease of that (186 mg/kg) in F4 in the river. Dollar et al. (2001) reported that the stability of metals in the residual fraction was unlikely to be affected by changes in pH and redox potential. In contrast, Peijnenburg and Jager (2003) noted that metals can transform in their availability or accessibility because of long-term changes in such parameters as organic matter content as well as pH and redox conditions. Moreover, it is reported that even the metals in residual fraction in soil samples was bio-accessible to a significant degree (Madrid et al. 2008). Therefore, some part of Mn in F4 in the Niitsu River could transform to the acid extractable and the oxidizable Mn because of these parameters. Furthermore, a part of Mn in F1 could have been lost by mobilization into the aquatic phase in the Niitsu River. This might cause a lower mean concentration (474 mg/kg) of Mn in the Niitsui River than that (506 mg/kg) in the Nodai River.

The mean concentrations (Table 1) and compositions of Fe in F1 and F3 in the Niitsu River were significantly higher than those in the Nodai River. Although no statistically significant difference was found in the means of Fe composition in F4 between the two rivers, the mean Fe concentration in the fraction in the Niitsu River was significantly higher than that in the Nodai River (Table 1). Moreover, the mean of the total Fe concentration (53,400 mg/kg) in the Niitsu River was significantly higher than that (27,800 mg/kg) in the Nodai River (Igari et al. 2012). In F1, F3 and F4, the excess (1,140, 2,730 and 18,800 mg/kg) of the mean concentrations of Fe in the Niitsu River to those in the Nodai River accounted respectively for 4.5, 11 and 73 % of the excess (25,600 mg/kg) of the total Fe concentration in the Niitsu River.

Among the investigated metals, Ni was the only metal for which the mean total concentration in the Nodai River was higher than that in the Niitsu River (Igari et al. 2012). The mean concentration and composition of Ni in F4 in the Niitsu River were significantly lower than those in the Nodai River. In contrast, those in F1–F3 in the Niitsu River were significantly higher than those in the Nodai River. Therefore, a part of Ni in F4 can transform to the other fractions in the Niitsu River (Madrid et al. 2008; Peijnenburg and Jager 2003). Moreover, F1 compositions of Ni showed an increasing tendency toward the downstream sites as described above, which implies that a part of Ni in the F1 had been lost by mobilization into the aquatic phase in the Niitsu River.

For Zn, the mean composition of Zn in F1 in the Niitsu River (36 %) was significantly higher than that in the Nodai River (11 %). The mean of the total Zn concentration in the Niitsu River (285 mg/kg) was also significantly higher than that in the Nodai River (115 mg/kg), which suggests that Zn derived from local sources in the Niitsu River Basin was mainly the acid-extractable phase. The excess (95 mg/kg) of the mean concentration of Zn in F1 (107 mg/kg) in the Niitsu River to that (12 mg/kg) in the Nodai River accounted for 56 % of the excess (170 mg/kg) of the total Zn concentration in the Niitsu River. Moreover, the excess (34 and 41 mg/kg) of the mean concentrations of Zn in F2 and F3 in the Niitsu River to those in the Nodai River accounted respectively for 20 and 24 % of the excess of the total Zn concentration in the Niitsu River. These additional Zn phases can also be derived from the local sources in the Niitsu River Basin.

Although no statistically significant difference was found in the means (Table 1) of Pb concentrations in F2 between the two rivers, the mean Pb composition (5.8 %) in F2 in the Niitsu River was significantly lower than that (31 %) in the Nodai River. In contrast, the mean Pb concentration (10 mg/kg) and composition (29 %) in F3 in the Niitsu River was significantly higher than those in the Nodai River where Pb was not detected in the fraction. Moreover, the mean of total Pb concentration in the Niitsu River (35 mg/kg) was significantly higher than that in the Nodai River (10 mg/kg), which suggests that the oxidizable Pb can be a major component derived from local sources in the Niitsu River Basin. The excess (10 mg/kg) of the mean concentration of Pb in F3 in the Niitsu River to that in the Nodai River accounted for 38 % of the excess (25 mg/kg) of the total Pb concentration in the Niitsu River.

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