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Extractability of Heavy Metals in Sediments and Farmland Soil in the To Lich and Kim Nguu River System

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The purpose of the present study was to evaluate the availability and mobility of heavy metals in sediments and farmland soils in the To Lich and Kim Nguu River system through the amount of heavy metals extracted with acids and its percentage to total metal concentration. Twelve sediment samples were collected from the To-Lich, Kim-Nguu River and 19 soil samples were collected at two different locations in agricultural field and pappy field along the river. The results showed that the highest amount of heavy metals extracted from the sediment samples with 0.5 M HCl and 0.1 M HNO₃ was in the order of Zn > Cr > Cu > Pb > Ni > Cd and Cr > Zn > Ni > Cu > Pb > Cd, respectively. The average percentage of the amount of extractable metals to the total metal concentration for the agricultural soil was the highest for Ni (70%), followed by Cr (65%), Cd (50%), Zn (20%), Pb (10%) and Cu (7%), suggesting that Ni is more labile and available to plants than other elements. The average percentage for the paddy soil was the highest for Cr (75%), followed by Ni (50%), Cd (40%), Zn (30%), Pb (20%) and Cu (15%), suggesting the highest availability of Cr to plants.

In general, the amount of the extracted heavy metals was similar between the agricultural and paddy soil. The amount of heavy metals extracted with 0.5 M HCl was greater than that extracted with 0.1 M HNO₃ for all metals except Cr.

Keywords: extracted heavy metals, availability of heavy metals, agricultural soils

INTRODUCTION

To predict the availability of heavy metals to plants, the extractability of heavy metals from soils and sediments with various chemical reagents has been assessed. Amacher (1996), and Filipek and Pawlowski (1990) recommended HCl as one of the extractants to estimate plant-available Ni, Cd, and Pb in soil. Yania *et al.* (1998) also showed that tenth molar (0.1 M) HCl had been widely used to evaluate the availability of heavy metals in soils and sediments.

The physiochemical characteristics of soil and sediment, and the type of acid for extraction influence the amount of heavy metals extracted. In addition, the ratio of soil and sediment to extractant solution is one of the most important factors that control the amount of heavy metals extracted. Many researchers used 1/5 for the ratio of solid to extractant solution in extracting heavy metals from soils and sediments using 0.1 M HCl and other acids.

There are two rivers in Hanoi City, the To Lich and Kim Nguu River, which are the main source of irrigation water for suburban agricultural land and fish farming pond. The industrial wastewater discharged into the rivers has degraded the quality of sediments in the river system. This has affected not only farming and fish breed-

ing, but also the health of general public in surrounding areas.

The present study was conducted to evaluate the availability and mobility of heavy metals in the sediments and agricultural soils in the To Lich and Kim Nguu River system through the amount of metals obtained by acid treatment and its percentage to total metal concentration.

MATERIALS AND METHODS

Materials

Twelve sediment samples (*SD*) were collected from the To-Lich and Kim-Nguu River and 19 soil samples were collected at two different locations: location 1 (agricultural field) and location 2 (pappy field) at Van Dien area of Hanoi City on December 3 to 6 of 2005 (Fig. 1). Sediment samples were collected from the surface zone (20 cm) of the sediment at the 12 sites submerged with water (Table 1). The core samples of 90 cm depth were also taken at 2 sites where sediment surface was exposed to the air.

Eight soil samples (*SS*) were collected from location 1– agricultural field from the depths of 0–20, 20–40 and 40–60 cm at the locations of various distances from the canal: 0, 20 and 60 m.

Another eleven soil samples were collected from location 2– paddy field near roadside at 0, 3, 5, 10, 20 and 50 m from the edge of the road (Table 2). Also samples were taken from the depths of 0–20 and 20–40 cm at the locations of various distances from the road: 0, 3, 6, 10, 20 and 50 m. They were brought to Japan after air – drying,

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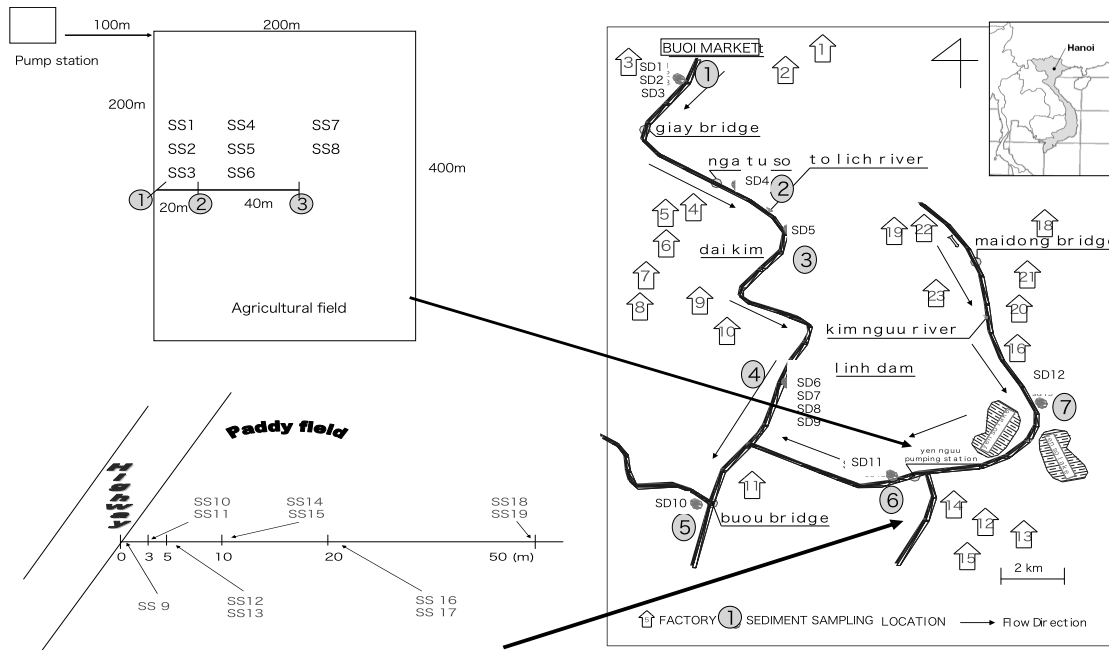


Fig. 1. Sampling location.

Table 1. Total concentrations of Cd, Cr and Cu in the sediment samples and the amount of metals extracted with acids (mg/kg)

No	Depth (cm)	Cd			Cr			Cu		
		Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃
SD 1	0–30	4.4	1.4	1.2	260	115	160	250	77	5
SD 2	30–60	5.3	3.0	2.4	320	120	181	441	64	3
SD 3	60–90	5.2	2.5	2.1	345	111	146	345	37	9
SD 4	0–20	20	10.1	12.6	472	112	143	478	105	6
SD 5	0–20	40	29.9	25.8	445	101	132	490	96	5
SD 6	0–20	2.7	2.8	2.2	357	121	158	422	64	9
SD 7	0–30	2.5	1.5	1.2	340	137	155	395	37	4
SD 8	30–60	3.7	2.6	1.7	220	131	152	370	48	21
SD 9	60–90	2.7	1.8	1.6	240	112	147	325	50	27
SD 10	0–20	8.5	5.5	3.6	401	115	159	324	52	28
SD 11	0–20	17	11.4	11.1	415	103	135	535	101	5
SD 12	0–20	3.5	2.4	1.9	475	105	141	520	114	5

Table 2. Total concentrations of Ni, Pb and Zn in the sediment samples and the amount of metals extracted with acids (mg/kg)

No	Depth (cm)	Ni			Pb			Zn		
		Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃
SD 1	0–30	65	24	17	368	58	6	250	201	26
SD 2	30–60	63	22	15	395	46	1	441	187	21
SD 3	60–90	48	15	10	425	42	2	345	173	18
SD 4	0–20	165	58	31	490	101	3	478	262	17
SD 5	0–20	108	44	25	450	46	3	490	223	31
SD 6	0–20	57	31	19	348	42	3	422	203	171
SD 7	0–30	52	14	15	280	28	1	395	83	98
SD 8	30–60	58	18	10	260	45	12	370	117	64
SD 9	60–90	50	19	11	370	52	12	325	106	55
SD 10	0–20	64	30	19	435	45	6	324	149	131
SD 11	0–20	142	44	32	430	212	1	535	241	207
SD 12	0–20	151	45	32	665	37	1	520	225	197

and then ground, passed through a 1-mm sieve, and preserved in plastic bottles.

Methods

Both 0.5 M HCl and 0.1 M HNO₃ were used to extract heavy metals from the sediments and agricultural soils. Heavy metal extraction was made on suspensions with the ratio of solid to extractant solution of 1:5. Five g air-dried sediment and soil, and 25 ml 0.5 M HCl and 0.1 M HNO₃ were used. The suspensions were agitated continuously for an hour and then centrifuged at 2,500 rpm for 10 min. The supernatant was separated and analyzed for the concentration of Cd, Cr, Cu, Ni, Pb and Zn by atomic absorption spectrophotometer (AAS).

For total metal concentration, heavy metals in the sediment was digested with 1 M HNO₃ at 96 °C for an hour and centrifuged, and dissolved metals in the supernatant were analyzed by atomic absorption spectrophotometer (Committee of Soil standard methods for Analyses and Measurement, 1986).

The determination of metal concentrations was made in duplicate and the relative deviation of the duplicate values was mostly less than 5%.

RESULTS AND DISCUSSIONS

Sediment samples

The amount of heavy metals extracted with 0.5 M HCl and 0.1 M HNO₃ are shown in Tables 1 and 2 along with the total heavy metals determined by the extraction with concentrated HNO₃ (Huong *et al.*, 2008). As a whole, the highest amount of metals extracted was in the order of Zn > Cr > Cu > Pb > Ni > Cd for 0.5 M HCl and of Cr > Zn > Ni > Cu > Pb > Cd for 0.1 M HNO₃.

The Cd extracted with 0.5 M HCl and 0.1 M HNO₃ was in an extremely wide range between 1.4 and 39.9 mg/kg and 1.2 and 25.8 mg/kg, respectively. The Cd extracted with 0.5 M HCl was slightly higher than that with 0.1 M HNO₃ in most samples. The extracted Cd for SD 4, 5 and 11 were much greater compared to other samples, which was as much as 50% of the total Cd concentration. A significant correlation coefficient was obtained between the extractable and total Cd for both acids in all samples. The greater extracted heavy metals in SD 4, 5 and 11 would be due to the higher total heavy metal concentrations. In general, the mobility and extractability of Cd in the sediment was very high.

The Cr extracted with 0.5 M HCl and 0.1 M HNO₃ was in a range of 101 to 137 mg/kg and 132 to 181 mg/kg, which was 15–20% of the total heavy metal concentration. The Cd extracted with 0.5 M HCl tended to be slightly smaller than that with 0.1 M HNO₃. There was not much difference in the amount of available heavy metals among the samples. The correlation between extractable and total Cd was not significant for both extractants.

The extracted Cu ranged from 37 to 105 mg/kg for 0.5 M HCl and 3 to 28 mg/kg for 0.1 M HNO₃, which was 10–30% and 1–10% of the total heavy metal concentration, respectively. The Cu extracted with 0.5 M HCl was 5 to 10 times greater than that with 0.1 M HNO₃. Much

difference in the amount of available heavy metals among the samples would be due to the difference in the extracted total heavy metals. A correlation between extractable and total concentration was not significant for both extractants.

In Table 2, the amount of extractable Ni and its percentage of total metal concentration were similar between 0.1 M HNO₃ and 0.5 M HCl with the range of 10–50 mg/kg and 20–50%. The correlation between the extractable metal and total metal concentration was significant for both extractants. The samples with higher total heavy metal concentrations gave higher amount of extracted Ni for SD 4, 5, 11, 12.

For the extracted Pb, big differences were found among the samples and between the extractants. The Pb extracted with 0.5 M HCl was 10 times greater than that with 0.1 M HNO₃. Extractable Pb was in a range of 28–212 mg/kg for 0.5 M HCl and 1–12 mg/kg for 0.1 M HNO₃, which was 10–20% and 1–5% of total Pb concentration, respectively. The correlation between extractable and total concentration was significant for 0.5 M HCl but not for 0.1 M HNO₃.

The amount of extracted Zn exhibited big differences among the samples for both extractants, with a range of 83–262 mg/kg for 0.5 M HCl and 17–207 mg/kg for 0.1 M HNO₃.

Soil samples

The total heavy metals concentration in the soil of suburban farmland in Hanoi indicates that the soil has been polluted with heavy metals through the irrigation of water from the To-Lich and Kim-Nguu River (Huong *et al.*, 2008 a, b). The amount of extractable heavy metals in the agricultural and paddy soil used for the above study is shown in Tables 3, 4, 5 and 6.

The amount of extracted heavy metals of agricultural soil (Table 3 and 4) extracted with 0.5 M HCl and 0.1 M HNO₃ was in the range of 2–3.3 mg/kg and 1.6–2.1 mg/kg for Cd, 108–124 mg/kg and 136–161 mg/kg for Cr, 20–45 mg/kg and 9–17 mg/kg for Cu, both 15–55 mg/kg for Ni, 21–46 mg/kg and 1–7.6 mg/kg for Pb, and 45–57 mg/kg and 21–45 mg/kg for Zn.

The heavy metals in paddy soils (Table 5 and 6) extracted with 0.5 M HCl and 0.1 M HNO₃ was in the range of 2–2.8 mg/kg and 1.6 to 2.4 mg/kg for Cd, 102–128 mg/kg and 137–155 mg/kg for Cr, 31–50 mg/kg and 5–25 mg/kg for Cu, 5–24 and 4–11 mg/kg for Ni, 15–38 mg/kg and 1–4 mg/kg for Pb, and 40–93 mg/kg and 11–41 mg/kg for Zn.

The average percentage of the amount of extractable metals to the total metal concentration for the agricultural soil was the highest for Ni (70%), followed by Cr (65%), Cd (50%), Zn (20%), Pb (10%) and Cu (7%), suggesting that Ni is more labile and available to plants than other elements. The average percentage for the paddy soil was the highest for Cr (75%), followed by Ni (50%), Cd (40%), Zn (30%), Pb (20%) and Cu (15%), suggesting the highest availability of Cr to plants.

In general, the amount of the extracted heavy metals was similar between the agricultural and paddy soil.

Table 3. Total concentrations of Cd, Cr and Cu in the soil samples of the agricultural field and the amount of metals extracted with acids (mg/kg)

No	Depth (cm)	Cd			Cr			Cu		
		Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃
SS 1	0-20	4.5	3.3	2.1	190	108	158	230	45	17
SS 2	20-40	4.0	2.0	1.9	190	134	161	200	29	12
SS 3	40-60	4.1	2.3	1.9	172	126	139	195	34	10
SS 4	0-20	4.0	2.3	1.9	170	112	145	218	40	15
SS 5	20-40	4.0	2.0	1.8	178	109	155	185	26	11
SS 6	40-60	3.7	2.0	1.6	145	104	136	170	32	10
SS 7	0-20	3.9	2.3	2.0	185	124	154	208	39	17
SS 8	20-40	3.9	2.2	1.6	172	115	145	162	20	9

Table 4. Total concentrations of Ni, Pb and Zn in the soil samples of the agricultural field and the amount of metals extracted with acids (mg/kg)

No	Depth (cm)	Ni			Pb			Zn		
		Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃
SS 1	0-20	80	55	18	145	46	0.9	263	57	45
SS 2	20-40	59	20	11	138	23	3.1	190	47	35
SS 3	40-60	65	21	12	135	29	5.0	195	52	22
SS 4	0-20	74	51	15	130	36	1.3	255	54	55
SS 5	20-40	56	41	11	132	20	5.0	183	46	30
SS 6	40-60	58	46	11	126	25	6.8	182	50	20
SS 7	0-20	45	16	9	125	33	6.6	187	56	27
SS 8	20-40	42	15	8	120	21	7.6	178	45	21

Table 5. Total concentrations of Cd, Cr and Cu in the soil samples of the paddy field and the amount of metals extracted with acids (mg/kg)

No	Depth (cm)	Cd			Cr			Cu		
		Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃
SS 9	0-20	7.5	2.0	1.8	201	110	146	270	50	25
SS 10	0-20	4.5	2.8	2.4	195	112	155	225	39	16
SS 11	20-40	4	2.1	1.9	190	121	154	245	25	10
SS 12	0-20	4.5	2.6	2.2	195	108	150	220	35	15
SS 13	20-40	3.5	2.2	2.1	178	106	145	190	31	9
SS 14	0-20	4.5	2.5	2.1	195	110	148	192	38	14
SS 15	20-40	3	2.1	2.0	166	102	140	175	32	7
SS 16	0-20	4	2.3	2.0	193	115	147	190	40	16
SS 17	20-40	2.9	2.1	1.8	165	116	140	165	35	7
SS 18	0-20	4	2.1	2.0	192	128	147	190	43	13
SS 19	20-40	3	2.0	1.6	162	120	137	155	36	5

Table 6. Total concentrations of Ni, Pb and Zn in the soil samples of the paddy field and the amount of metals extracted with acids (mg/kg)

No	Depth (cm)	Ni			Pb			Zn		
		Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃	Total	0.5 M HCl	0.1 M HNO ₃
SS 9	0-20	58	13	6	195	38	2	310	93	41
SS 10	0-20	56	24	11	175	36	1	256	84	38
SS 11	20-40	40	7	8	160	20	4	165	49	17
SS 12	0-20	51	23	10	165	35	1	200	80	34
SS 13	20-40	40	8	9	155	20	3	165	46	15
SS 14	0-20	50	20	8	165	33	1	183	77	31
SS 15	20-40	37	8	7	145	19	4	163	45	15
SS 16	0-20	48	19	7	160	31	1	175	74	26
SS 17	20-40	36	7	6	140	17	4.0	163	43	13
SS 18	0-20	46	15	7	155	30	1.0	165	71	21
SS 19	20-40	32	5	4	130	15	3	162	40	11

The amount of heavy metals extracted with 0.5 M HCl was greater than that extracted with 0.1 M HNO₃ for all metals except Cr.

CONCLUSIONS

The amount of heavy metals extracted from the river sediments and farmland soil depended on the type of extractants and heavy metals. The highest amount of heavy metals extracted from the sediment samples was in the order of Zn > Cr > Cu > Pb > Ni > Cd for 0.5 M HCl and Cr > Zn > Ni > Cu > Pb > Cd for 0.1 M HNO₃. In general, the amount of extracted heavy metals was similar between agricultural and paddy soils. The amount of heavy metals extracted with 0.5 M HCl was greater than that extracted with 0.1 M HNO₃ for all metals except Cr.

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