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Sequential Fractionation of Copper, Nickel, Lead, and Zinc in Agricultural Soils and River–Sediment in Tuliem and Thanhtri Districts of Hanoi City, Vietnam

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Sequential fractionation was applied to partition heavy metals in the agricultural soils and river–sediment taken from Tuliem and Thanhtri districts of Hanoi city. Although there was observed a considerable variation among the heavy metals in the proportion of various fractions, Pb showed the similar percentage of each fraction between the agricultural soils and river–sediment, and the Fe–Mn oxides and residual fractions overwhelmingly dominated over the other three fractions. In the speciation of Cu, one agricultural soil which was supposed to be polluted with Cu showed the relatively high percentage of the Fe–Mn oxides fraction. In the river–sediment Cu was occupied with the organic fraction in around 70%. In Ni and Zn, the river–sediment showed the high proportion of the exchangeable and carbonates fractions. The sum of both fractions was about 25 and 30% for Ni and Zn, respectively, while it was quite low in the agricultural soils. Mobility of heavy metals in the river–sediment was estimated to be in the sequence of Ni, Zn>Cu>Pb. Based on its higher mobility along with the high total content in the river–sediment, the first priority should be placed on Zn from the viewpoint of the control of heavy metal pollution.

INTRODUCTION

In recent years increased industrialization and population growth have led to progressively increasing fluxes of many heavy metals to soil and river in Hanoi city, Vietnam. In the previous paper (Ho and Egashira, 1999), the authors investigated the heavy metal status of the agricultural soils and river–sediment taken from Tuliem and Thanhtri districts of Hanoi city. Accumulation of several kinds of heavy metals was noticed in the river–sediment of the Kimnguu River, in contrast to the agricultural soils being in the normal range of the heavy metals examined, except for one upland soil cultivated for vegetables throughout the year in which Cu pollution was suspposed.

In most studies dealing with heavy metals, only total contents have been reported, to give an information concerning possible enrichment in soils. However, total content of heavy metals is not enough to estimate toxicity and mobility of them in soils and sediments. A knowledge of distribution of heavy metals among various forms or chemical forms of heavy metals associated with particulates is essential for estimating biological availability or physicochemical reactivity of heavy metals in soils and sediments. Heavy metals may be complexed with organic compounds, adsorbed or occluded in carbonates or oxide minerals or in the structure of primary and secondary minerals (Hickey and Kittrick, 1984).

The objective of the present study was to determine the chemical partition of Cu, Ni, Pb, and Zn in the river–sediment in comparison with agricultural soils, both taken from

Tuliem and Thanhtri districts of Hanoi city. Three soils and one river–sediment were selected for this purpose from the samples used in the previous study (Ho and Egashira, 1999). The samples were subjected to sequential fractionation and the heavy metals were partitioned into five operationally defined fractions: exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, and residual.

MATERIALS AND METHODS

1. Location and samples

Samples selected for the present study are briefly described in Table 1. Sampling sites of soils and river–sediment and the river system in Tuliem and Thanhtri districts of Hanoi city were indicated in the previous paper (Ho and Egashira, 1999). Three soil samples are as follows: sample No.1 is supposed to be polluted with Cu; samples No.4 and No.6 are in the normal range of heavy metals and were selected as a representative of agricultural soils of Tuliem and Thanhtri districts, respectively. The river–sediment is a sample from the Kimnguu River and was found to be highly accumulated with different heavy metals.

2. Sequential fractionation of heavy metals

Determination of speciation or distribution of Cu, Ni, Pb, and Zn in soil and river–sediment was made by the Tessier *et al.* (1979) sequential chemical extraction scheme (Fig. 1). One gram of sample was used and extractions were carried out directly in 50–mL polypropylene Nalgene centrifuge tubes to minimize losses of solid material. Residues were separated from the supernatant by 30 min centrifugation at 10,000 min^{-1} speed. The residue was washed with 8 mL of water followed by hand shaking and then followed by 30 min centrifugation before the next extraction. Metal content of the five fractions in the filtered solution was determined by atomic absorption spectrometry. Determination was made in duplicate and the relative deviation of the duplicate values was usually less than 5%. Due to no contamination of Mn, low confent of total Cd in agricultural soils, and a close similarity of Cr with Ni (Ho and Egashira, 1999), these three metals were not considered in the present study.

Table 1. Brief description of agricultural soils and river–sediment used in the study.

Sample No.	Location		Land use (crop)	Relative land height in the region	Soil classification by FAO/UNESCO
	District	Commune			
1	Tuliem	Taytuu	Upland (vegetables)	High	Orthi–Umbri–Eutric Fluvisols
4		Yenhoa	Paddy (rice–rice)	Lowest (marshy)	Epi–Stagni–Eutric Gleysols
6	Thanhtri	Thanhliet	Paddy (rice–rice)	Middle	Orthi–Plinthi–Eutric Fluvisols
10		Tranphu	–	River bed	–

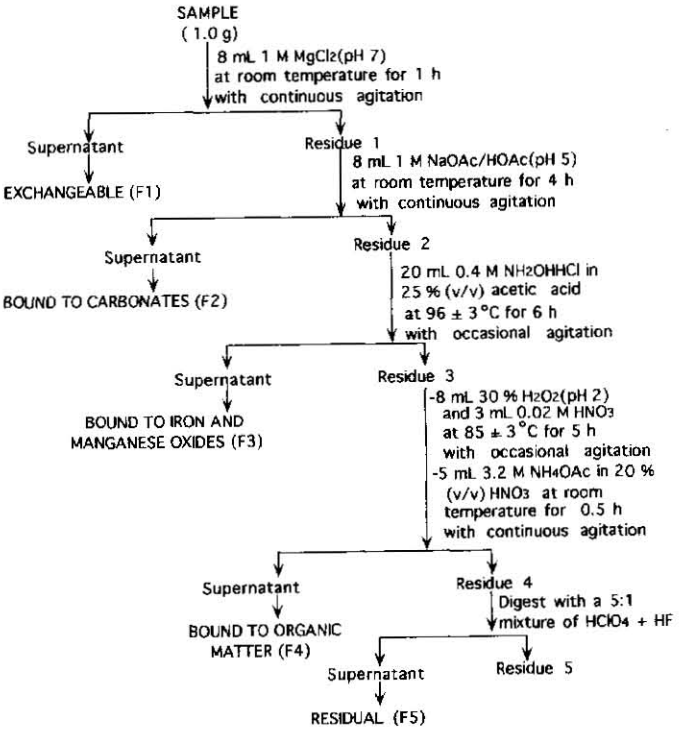

Fig. 1. Sequential fractionation scheme for the speciation of heavy metals.

RESULTS

Total heavy metal contents

Contents of total Cu, Ni, Pb, and Zn for the agricultural soils and river-sediment are reproduced in Table 2 (Ho and Egashira, 1999). Contents of the total heavy metals were regarded to be in the normal range for the agricultural soils, except for Cu in sample No.1. In contrast, the river-sediment of the Kimnguu River flowing through the area contained large amounts of total Zn, Cu, Pb, and Ni, and order of the content was Zn>Cu>Pb>Ni.

Speciation of heavy metals

Contents of sequentially fractionated heavy metals are given in Table 3. Total of the contents of five fractions is expected to be equal to the total content listed in Table 2. However, the former amounted only to 62–82, 78–97, 72–89, and 62–83% of the latter for Cu, Ni, Pb, and Zn, respectively. A possible reason to be below 100% is underestimation of the content of the residual fraction due to the difference between procedures used for

Table 2. Contents of total heavy metals in agricultural soils and river-sediment (mg kg^{-1}).

Sample No.	Cu	Ni	Pb	Zn
1	73.2	33.6	31.9	114.5
4	50.0	45.6	45.1	116.9
6	43.0	66.0	45.3	137.2
10	258	145.5	157.5	1040

(Oven dry basis)

Table 3. Contents of sequentially fractionated heavy metals in agricultural soils and river-sediment (mg kg^{-1}).

Sample No.	Fraction	Cu	Ni	Pb	Zn
1	Exchangaeble	ND	1.0	1.0	ND
	Bound to carbonates	1.4	1.3	1.0	4.5
	Bound to Fe–Mn oxides	25.1	11.2	13.3	42.5
	Bound to organic matter	8.9	4.6	2.9	4.0
	Residual	18.8	14.5	10.2	36.3
		(37.8)	(15.5)	(13.7)	(63.5)
4	Exchangaeble	ND	0.9	1.3	ND
	Bound to carbonates	0.2	1.2	1.9	0.4
	Bound to Fe–Mn oxides	9.3	10.6	19.4	27.2
	Bound to organic matter	8.8	4.0	2.9	4.5
	Residual	17.9	20.8	12.7	51.7
		(31.7)	(28.9)	(19.6)	(84.8)
6	Exchangaeble	ND	1.4	0.6	0.1
	Bound to carbonates	ND	1.5	1.3	4.1
	Bound to Fe–Mn oxides	4.4	16.4	19.2	27.3
	Bound to organic matter	4.4	5.9	3.1	6.1
	Residual	17.9	26.3	9.9	47.3
		(34.2)	(40.8)	(21.1)	(99.6)
10	Exchangaeble	6.2	11.1	0.7	46.6
	Bound to carbonates	9.1	21.0	3.7	249
	Bound to Fe–Mn oxides	15.2	65.6	72.2	485
	Bound to organic matter	164.6	13.0	6.5	41.6
	Residual	16.6	12.8	29.9	36.2
		(63)	(34.8)	(74.4)	(218)

(Oven-dry basis)

ND: not detected.

The values in the parenthesis are the content of the residual fraction calculated as the difference between the total content listed in Table 2 and the total of the contents of four fractions excluding the residual fraction.

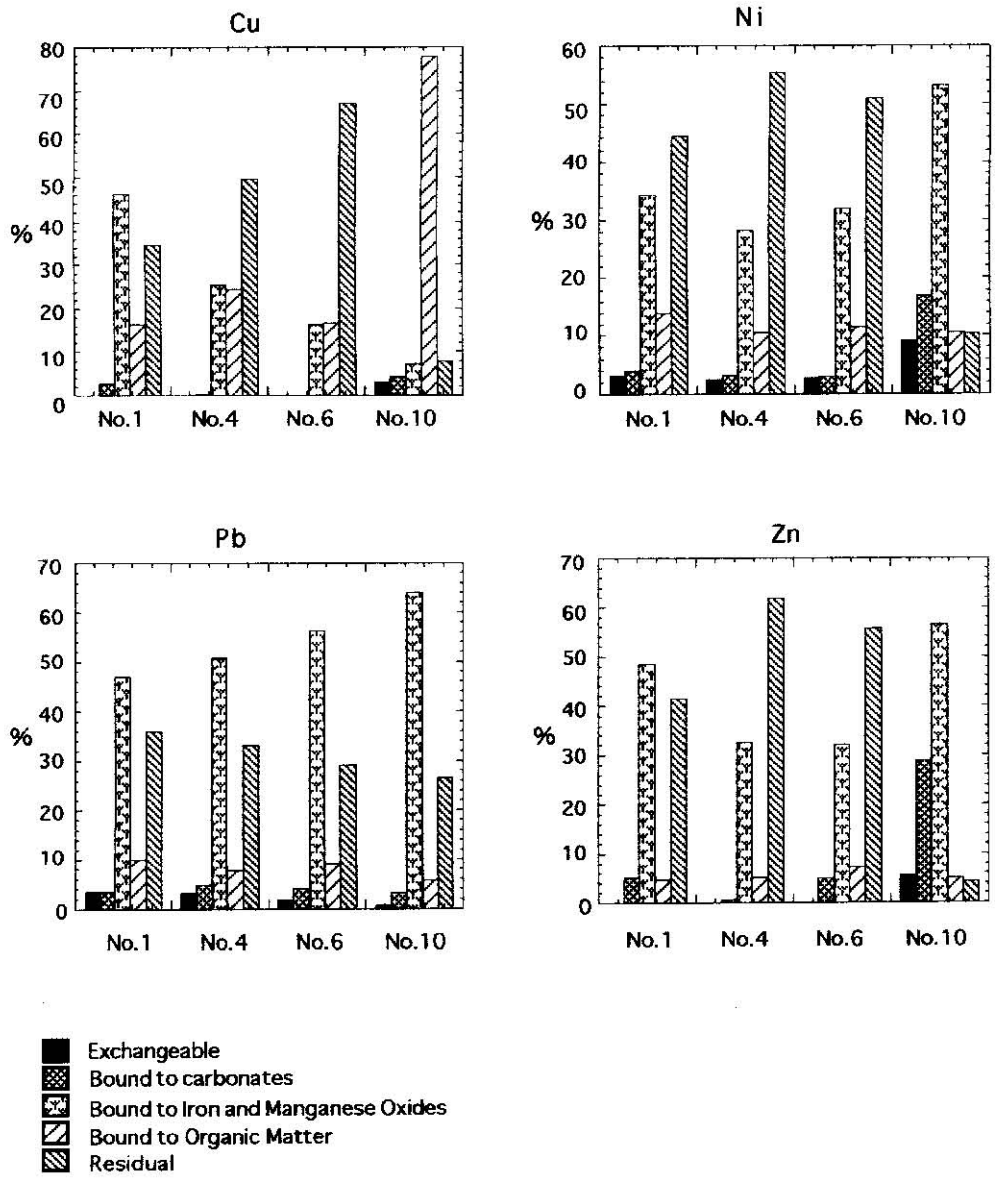

Fig. 2. Percentages of Cu, Ni, Pb, and Zn associated with each of five sequential fractions for agricultural soils and river-sediment, in which the content of the residual fraction measured by the sequential fractionation illustrated in Fig. 1 was used as such.

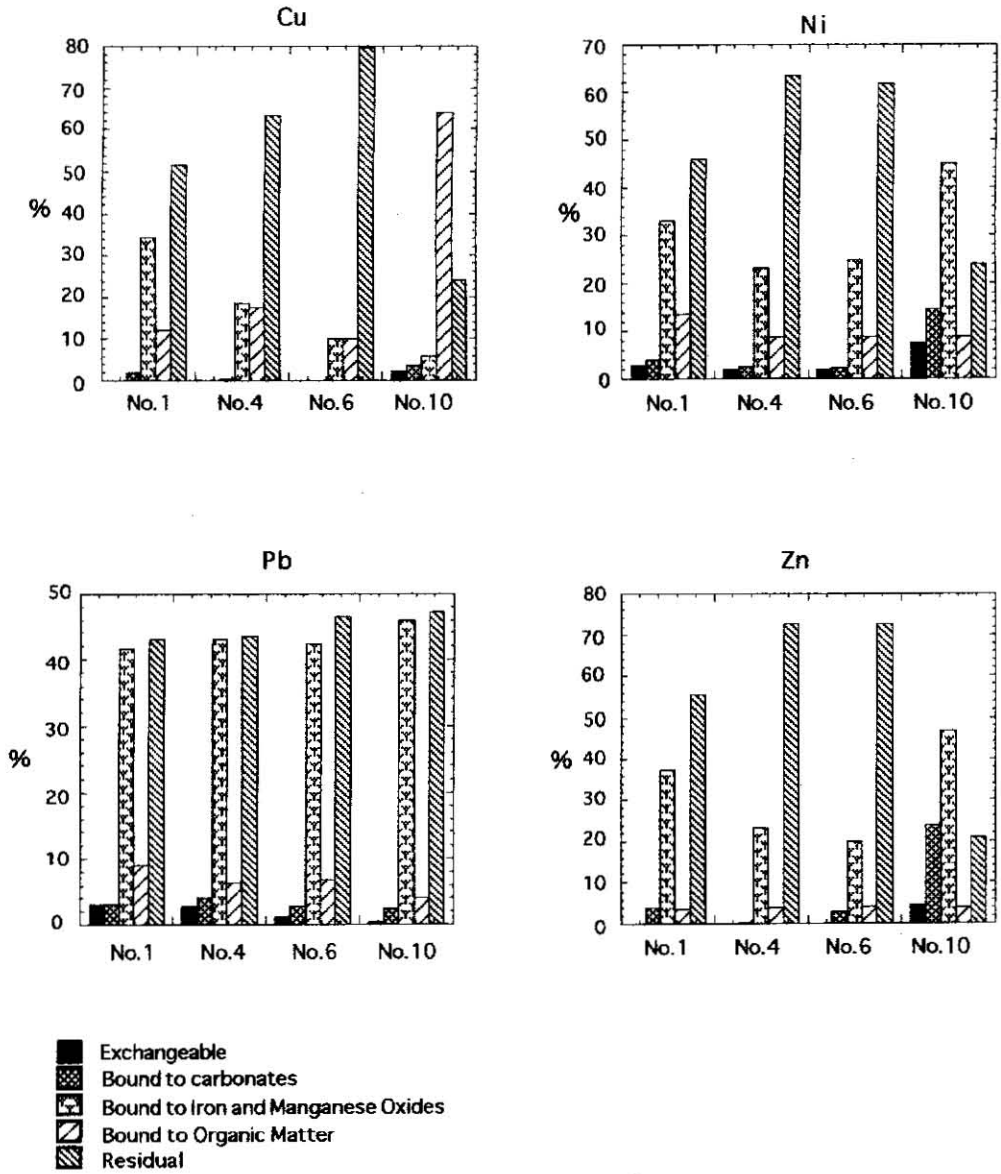

Fig. 3. Percentages of Cu, Ni, Pb, and Zn associated with each of five sequential fractions for agricultural soils and river-sediment, in which the content of the residual fraction calculated as the difference between the total content and the total of the contents of four fractions excluding the residual fraction was used as such.

the measurement of the residual fraction and the total content. In this context, the content of the residual fraction was calculated as the difference between the total contents listed in Table 2 and the total of the contents of four fractions excluding the residual fraction and is shown in the parenthesis of Table 3.

Percentages of heavy metals associated with each of five sequential fractions for agricultural soils and river–sediment were calculated using two values for the residual fraction, and are illustrated in Figs. 2 and 3. Percentages of each fraction were different between the two figures, but general tendency was found to be similar to each other.

a) Copper

Among the agricultural soils, samples No.4 and No.6 showed the highest proportion of the residual fraction, occupying 50–63 and 67–80% of the total, respectively. The Fe–Mn oxides and organic fractions followed the residual fraction and showed the similar percentage to each other. The exchangeable fraction was not detected and the carbonates fraction accounted for not detected to 0.4–0.6%. In comparison to samples No.4 and No.6, sample No.1 which is possibly polluted with Cu showed the significantly high proportion of the Fe–Mn oxides fraction. The exchangeable fraction was not detected and the carbonates fraction accounted for 1.9–2.6%. Copper added to soil may quickly move to the Fe–Mn oxides fraction and slowly change to the residual fraction.

The river–sediment collected from the Kimnguu River showed the quite high proportion of the fraction associated with organic matter. The organic fraction was in 64–78%. The high proportion of the organic fraction can be partially ascribed to the high organic matter content of the river–sediment (Ho and Egashira, 1999). In addition, organic compounds under the reduced condition may be more active to bind with Cu. According to Tessier *et al.* (1980) Cu exhibited the highest stability constants for the most ligands of all the metals considered. The high affinity of organic ligands makes Cu more stable in the river bed, leading to the suppression of diffusion or dispersion of Cu.

b) Lead

Distribution of Pb in the agricultural soils and river–sediment followed entirely the same order: Fe–Mn oxides≥residual>organic>carbonates>exchangeable. The fraction of Fe–Mn oxides occupied about 40–60% of the total Pb. The highest proportion of the Fe–Mn oxides fraction was reported by Tessier *et al.* (1980), Ramos *et al.* (1994) and Ma and Rao (1997) for soils and sediments highly concentrated or polluted with heavy metals, although the percentage of the Fe–Mn oxides fraction and the sequence following the Fe–Mn oxides fraction varied with soils and sediments. Lead added to soil or sediment may react selectively with Fe–Mn oxides and quickly move to the stable form. The sum of the exchangeable and carbonates fractions only represented 3–4 to 7–9% of the total Pb, and rather lower for the river–sediment. Association of Pb with Fe–Mn oxides in the river–sediment may prevent Pb from diffusion or dispersion to environment.

c) Nickel

Speciation of Ni was different between agricultural soils and river–sediment. The order was residual> Fe–Mn oxides> organic> carbonates, exchangeable for the agricultural soils and Fe–Mn oxides>carbonates>organic, exchangeable, with variation of residual, for the river–sediment.

The residual fraction accounted for 44–46 to 55–64% of the total Ni for agricultural soils while 10–24% for river-sediment, although Tessier *et al.* (1980) and Hickey and

Kittrick (1984) reported that majority of Ni in soils and sediments highly concentrated or polluted with heavy metals was in the residual fraction. The exchangeable and carbonates fractions were 8–9 and 14–17%, respectively, for the river–sediment. The higher proportion of the easily extractable forms of Ni is a characteristic of the river–sediment. Continuous addition of the river–sediment to agricultural field may become a source of Ni pollution to crops growing on the field.

d) Zinc

Because of a close relationship between Zn and Ni (Ho and Egashira, 1999), speciation of Zn was similar to that of Ni and clearly different between agricultural soils and river–sediment. Zinc in each fraction generally followed the following order: residual >Fe–Mn oxides>organic>carbonates>exchangeable for the agricultural soils; Fe–Mn oxides>carbonates>exchangeable, organic, with variation of residual, for the river–sediment. Although there was considerable variation with soils in the proportion to the total Zn in various fractions, Zn was primarily in the residual or Fe–Mn oxides fraction in agricultural soils.

In the river–sediment, the highest proportion was obtained in the Fe–Mn oxides fraction, with the residual fraction being 4–21%. Tessier *et al.* (1980), Kuo *et al.* (1983) and Hickey and Kittrick (1984) showed that Zn was primarily associated with Fe–Mn oxides in soils and sediments highly concentrated or polluted with heavy metals. The exchangeable fraction was essentially not detected in agricultural soils but 4–5% for river–sediment. The carbonates fraction was 0.3–0.5 to 4–5% and 24–29% for agricultural soils and rive–sediment, respectively. The sum of the exchangeable and carbonate fractions amounted to as high as 28–34% for the river–sediment. The relatively high proportion of the easily extractable forms suggests the high mobility of Zn and a possible source of the river–sediment as Zn pollution to crops.

DISCUSSION

From the viewpoint of assessment to the environmental impact of soils and sediments polluted with heavy metals, speciation of heavy metal as well as its total content is necessary. Total contents of different heavy metals of the agricultural soils and river–sediment taken from Tuliem and Thanhtri districts of Hanoi city was assessed in the previous paper (Ho and Egashira, 1999). In the present study, speciation of Cu, Ni, Pb, and Zn was assessed by the sequential extraction with distribution into five fractions: exchangeable, bound to carbonates, bound to Fe–Mn oxides, bound to organic matter, and residual. In agricultural soils with a normal range of the total heavy metal contents, the highest proportion was observed in the residual or Fe–Mn oxides fraction, depending on the heavy metals. This indicates the intimate association of heavy metals with clay particles or Fe–Mn oxides, suggesting the existence of heavy metals as the stable form in agricultural soils, and is comparable with the significant and positive correlations between total metal content and clay and/or free Fe_2O_3 contents observed for several heavy metals in the previous study (Ho and Egashira, 1999). The organic fraction was in the third position, ranging from 4 to 24%. The carbonates fraction was less than 5% and the exchangeable fraction was essentially not detected. Initially adsorbed heavy metals are retained in the exchangeable form and may pass into more specific and stable forms with

time (Beckett, 1989).

In the river–sediment which was highly accumulated with different heavy metals, speciation of heavy metals was different from that of the agricultural soils and varied with heavy metals (Figs. 2 and 3). In case of Cu, the highest fraction was the organic fraction with a percentage of around 70%. The content of Cu extracted as the organic fraction was higher by about 20–40 times for the river–sediment than for the agricultural soils, but the content of Cu extracted as the residual fraction was the same between them (Table 3). This suggests that Cu added to the river as industrial discharge was deposited and preferentially reacted with organic compounds, due to the high affinity of Cu to organic ligands, in the river–sediment. Very small portions of Cu added existed as the exchangeable, carbonates or Fe–Mn oxides form. Distribution of Pb into the five fractions was essentially the same between agricultural soils and river–sediment (Figs. 2 and 3). The contents of each fraction, except for the exchangeable fraction, of the river-sediment was higher by 2–4 times than those of the agricultural soils (Table 3), indicating that Pb added as industrial discharge was distributed in a fixed proportion into different fractions. This suggests that Pb has the highest affinity to solid particles in soils and sediments and quickly move to the ultimate distribution.

Distribution of Ni and Zn in the river–sediment was similar to each other and clearly different from that of the agricultural soils. In agricultural soils the proportion of the residual fraction was highest followed by the Fe–Mn oxides fraction, whereas in the river–sediment the proportion of the Fe–Mn oxides fraction was highest followed by the carbonates fraction, and the residual fraction was 10–24 and 4–21% for Ni and Zn, respectively (Figs. 2 and 3). The contents of both metals in the sequentially–fractionated residual fraction in the river–sediment were equal to or even below those in the agricultural soils (Table 3). The contents of the other four factions were always higher for the river–sediment than for the agricultural soils. Among the four fractions, increasing rate was extraordinarily high for the exchangeable and carbonates fractions. This indicates that considerable parts of Ni and Zn added as industrial discharge exist in the easily extractable and more mobile forms in the river–sediment. From this viewpoint, Ni and Zn are more probable pollutants to agricultural soils and water. Its higher mobility along with the highest content in the river–sediment (Table 2) suggests that the first priority should be placed on the control of Zn in the industrialized and densely–populated area of Tuliem and Thanhtri districts in Hanoi city.

CONCLUSIONS

Speciation or distribution into different fractions of Cu, Ni, and Zn in the river–sediment which was highly concentrated or polluted with various heavy metals was different from that of agricultural soils having a normal range of the total heavy metal contents. Copper was mostly associated with the organic fraction but considerable parts of Ni and Zn existed in the exchangeable and carbonates fractions. Based on the higher mobility and the high total content, Zn is the most serious pollutant to agricultural soils and water in Tuliem and Thanhtri districts of Hanoi city.

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