

Levels and Chemical Forms of Heavy Metals in Soils from Red River Delta, Vietnam

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Abstract Levels and chemical forms of heavy metals in forest, paddy, and upland field soils from the Red River Delta, Vietnam were examined. Forest soils contained high Cr and Cu levels that were higher in subsurface than in surface layers. Levels of Cu, Pb, and Zn that exceeded the limits allowed for Vietnamese agricultural soils were found in the surface layer of a paddy field near the wastewater channel of a copper casting village. High amounts of Zn accumulated in the surface soil of paddy fields close to a fertilizer factory and an industrial zone. In these cases, larger proportions of Cu, Pb, and Zn were found in the exchangeable and acid-soluble fractions compared to the low-metal soils. We conclude that no serious, large-scale heavy metal pollution exists in the Red River Delta. However, there are point pollutions caused by industrial activities and natural sources.

Keywords Chemical forms · Heavy metals · Pollution · Soil · Red River Delta · Vietnam

1 Introduction

The concentration of metals in uncontaminated soil depends primarily on the parent material from which the soil was formed. Significant increases of heavy metal concentrations in soils may occur as consequences of anthropogenic activities such as mining and smelting activities, electroplating, and the large-scale application of fertilizers, fungicides, pesticides, amended sewage sludge, etc. (Alloway 1990; Liu et al. 2007; Amir et al. 2005; Chen et al. 2007). Consequently, accelerated industrialization and urbanization have to be considered responsible for increasing heavy metal contents in soils (Huang et al. 2007; Khan et al. 2008; Zhao et al. 2007).

The total contents of heavy metals provide information on the accumulation of heavy metals in soils. However, the mobility of metals in agricultural soils, frequently characterized through available content and speciation, is more important in terms of metal toxicities to soil organisms and plants and of the impact on water systems. Metals from anthropogenic sources tend to be more mobile than pedogenic or lithogenic ones (Chlopecka et al. 1996; Karczewska 1996). Therefore, the readily mobile, soluble, exchangeable, and chelated fractions of the total heavy

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metal contents are of the greatest environmental interest (Kabata-Pendias and Pendias 1992; Chen et al. 2007).

In the Red River Delta, Vietnam, the rapid intensification of industrial activities including copper and lead casting, phosphorous fertilizer production, chemical manufacturing, etc., has been indicated to have introduced heavy metals into water and soil systems (Ho et al. 1998; Ho and Egashira 2001; Trinh and Wada 2004; Le 2002). The extent of soil Cd contamination in the delta region was reported to be more serious in suburban than in urban areas, which was ascribed to discharges from traditional handicraft production in rural villages (Trinh and Wada 2004).

Traditional products, for example pottery, ceramic, silk, carpentry, and fine art items from copper and aluminum, are manufactured in handicraft villages in rural areas of the Red River Delta. Most local residents take part in the production process during phases of low agricultural labor demand. This local production system has existed for a long time without any treatment of discharged wastewater. In fact, our interviews with village inhabitants indicated that many villagers had suffered from lung and liver cancer. Few previous studies reported the status of soils in traditional handicraft villages and the suburban areas around Hanoi city, Vietnam. Moreover, these studies mainly addressed total metal concentrations in the soils (Ho and Egashira 2001; Trinh and Wada 2004; Le 2002); no detailed investigation of contents and chemical forms of heavy metals in soils of the Red River Delta has been conducted so far. As it is the chemical form of a pollutant rather than its total concentration in the soil that determines its mobility and therefore the potential environmental risk, data of metal speciation in Red River Delta soils are desirable. For such studies, the sequential extraction method has been recommended to assess the origin and potential risk of polluted soils (Kabata-Pendias and Pendias 1992; Karczewska 1996).

To evaluate the influence of industrial zones and traditional handicraft villages on the levels of heavy metals in agricultural soils of the Red River Delta as well as the potential risks connected to these contamination sources, we studied heavy metal contents of soils, including (1) an assessment of the current status with respect to Cd, Cr, Cu, Pb, and Zn contents and (2) an evaluation of the chemical forms and the mobility of the heavy metals in the soils.

2 Materials and Methods

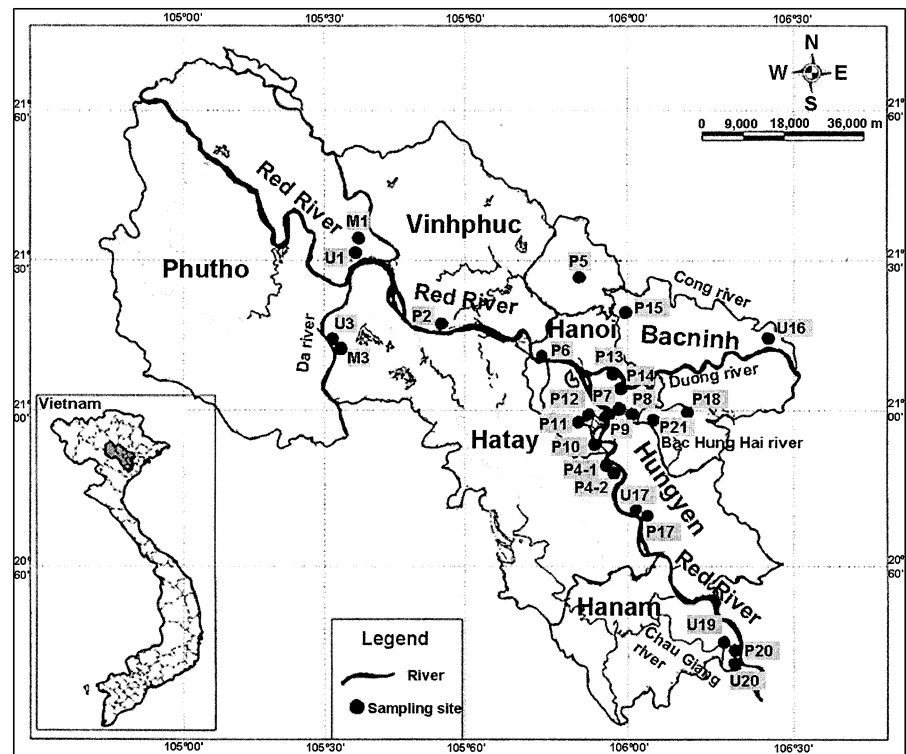
2.1 Sampling

Surface (0–5 cm) and subsurface (20–25 cm) soil samples were collected in March 2005 from two forest (F), 18 paddy (P), and six upland (U) fields in seven provinces located at both sides of the Red River (Fig. 1). The sampling sites were selected to cover areas without influence of contaminated groundwater or industrial activity, as well as areas with a known high potential of As contamination in the groundwater (Berg et al. 2001; Chander et al. 2004) and areas located in the vicinity of industrial zones and handicraft villages. An overview of our partial results regarding As contents in soils was provided by Phuong et al. (2008). The possible heavy metal contamination sources in each sampling area are listed in Table 1. The soil samples were air-dried, ground with a ceramic pestle, passed through a 2.0-mm sieve, and stored in plastic bottles until analysis.

2.2 Analytical Methods

For the determination of total contents of heavy metals (Cd, Cr, Cu, Pb, and Zn), the soil samples were digested in a mixture of HNO₃ and HF (9:1) by microwave heating (Multiwave, Perkin-Elmer, Yokohama, Japan). HCl-extractable heavy metals were obtained by extracting 5 g of soil with 25 mL 0.1 mol L⁻¹ HCl for 1 h at 30°C (Komai 1981; Baker and Amacher 1982; Jones et al. 1975). Chemical forms of heavy metals were estimated by the sequential extraction method reported by Iwasaki et al. (1997) with some modification. The reagents employed and shaking periods for the extraction of the seven different fractions of soil heavy metals are summarized in Table 2. The fractions were designated as water-soluble (Ws), exchangeable (Ex), acid-soluble (Aci), Mn oxide-occluded (MnO), organically bound (OM), Fe oxide-occluded (FeO), and residual (Res) fractions. Five milliliter conc. HClO₄, 10 mL conc. HNO₃, and 15 mL conc. HF were used to digest the residue fraction. The total concentrations of heavy metals in the acid digests and in the fractions were measured by atomic absorption spectrometry (AA-6800; Shimadzu, Kyoto, Japan). All chemicals used for the analyses were of analytical grade quality (Wako Pure Chemical Industries, Osaka, Japan).

Fig. 1 Location of sampling sites



3 Results

General physicochemical properties of the soils were summarized in Table 3 (Phuong et al. 2008). Based on the FAO classification system, the forest soils were classified as xanthic ferralsols, and the soils from paddy and upland fields were mostly fluvisols. The pH values of the forest field soils were strongly or very strongly acidic (4.7–5.3) while varied from slightly acidic to moderately alkaline (6.1–8.4) in most paddy and upland field soils.

3.1 Total and HCl-Extractable Heavy Metals

The ranges and means of total and HCl-extractable metal contents in surface and subsurface soils grouped by land use (forest, paddy, and upland fields) or by potential contamination sources are provided in Table 4. Generally, the total contents of Cr in forest soils were higher than in most paddy and upland soils. The *t* test was carried out to compare surface and subsurface layers of paddy and upland soils or soils without (group I) and with potential contamination source (group II). For the surface layer, the mean contents of total Cd and Zn in paddy soils were

significantly higher than in upland soils. In paddy soils, the mean contents of total Cd and Zn in the surface layer exceeded that in the subsurface layer significantly. On the other hand, in the surface layer, the mean content of total Cd in group II was significantly higher than in group I. Within group II, the mean content of total Cd was higher in the surface than in the subsurface layer. Except for these cases, no significant differences were observed between the surface and subsurface layers or groups of soils (*t* test, $P < 0.05$).

On average, the amount of HCl-extractable Cd in the soils corresponded to 53% of the total content. This proportion was lower for the other metals: Cu (15%), Pb (11%), Zn (8.8%), and Cr (0.6%). In surface and subsurface layers, the HCl-extractable contents of all metals were higher in paddy than upland soils, except for Cd in the subsurface. In paddy soils, HCl-extractable Cd in the surface layer significantly exceeded that in the subsurface layer. HCl-extractable contents of Cd, Cr, and Zn in the surface soils of group II were significantly higher than in the surface soils of group I. Moreover, for the subsurface layer, the amounts of HCl-extractable Cr, Cu, Pb, and Zn in soils from group

Table 1 List of sampling sites

Symbol	Location	Potential source of heavy metal pollution
Group I: Agricultural soil (no known potential pollution source)		
M1	Phutho	None
U16	Bacninh	None
U17	Hungyen	None
U19	Hanam	None
U20	Hanam	None
P6	Hanoi	None
P7	Hanoi	None
P17	Hungyen	None
P20	Hanam	None
Group II: Agricultural soil near potential contamination source		
M3	Hatay	Abundant Cu and pyrite minerals
U1	Phutho	Discharged wastewater from chemical and fertilizer factory
U3	Hatay	Irrigation water from Da river (upstream of Red river)
P2	Vinhphuc	Wastewater from a carpentry handicraft village
P4-1	Hatay	Wastewater from a traditional lacquer handicraft village
P4-2	Hatay	Wastewater from a traditional lacquer handicraft village
P5	Hanoi	Discharged wastewater from a solid waste treatment zone
P8	Hanoi	Discharged wastewater from a traditional ceramic handicraft village
P9	Hanoi	Irrigation water from Yen So lake containing discharged wastewater from Hanoi city
P10	Hanoi	Discharged wastewater from phosphorus fertilizer factory
P11	Hanoi	Irrigation water from Kimnguu river (subsidiary stream of Red river) containing discharged wastewater from Hanoi city
P12	Hanoi	Irrigation water from Kimnguu river (subsidiary stream of Red river) containing discharged wastewater from Hanoi city
P13	Hanoi	Discharged wastewater from chemical and fertilizer factory
P14	Hanoi	Discharged wastewater from industrial zone
P15	Bacninh	Discharged wastewater from aluminum and copper casting handicraft village
P18	Hungyen	Discharged wastewater from copper casting handicraft village
P21	Hungyen	Discharged wastewater from industrial zone

II significantly exceeded those in group I. On the other hand, the contents of HCl-extractable Cd in group II was significantly higher in the surface than in the subsurface layer. No other significant differences were observed between the surface and subsurface soil layers or groups of soils (t test, $P < 0.05$).

Total and HCl-extractable contents of heavy metals of the soils from groups I and II are given in Figs. 2a, 3, 4, 5, and 6a. In addition, box plots of the total contents of the selected heavy metals are shown in Figs. 2b, 3, 4, 5, and 6b. Values that exceeded the third quartile by a factor of 1.5 and values that were smaller than the first quartile divided by 1.5 were considered outliers and are labeled in the plots.

Cadmium Half of the surface soil samples from paddy fields in group II contained total Cd levels higher than those in group I (Fig. 2a). The differences between groups I and II of the upland or forest soils were insignificant (Fig. 2a). In the most extreme case, paddy field P10, the total Cd content (1.28 mg kg^{-1}) in the surface layer was five times higher than in the subsurface layer. The median of total Cd content of all soils was 0.30 mg kg^{-1} for the surface layer and lower than the detection limit in the subsurface soil (Fig. 2b). The highest proportions of HCl-extractable Cd, around 83% of the total content, were detected in both soil layers of paddy field P4-1 and in the surface layer of site P4-2; in most other samples, the proportion was less than 60%.

Chromium Figure 3a indicates that the total Cr content in forest field soils of group II (site F3) were higher than those of group I, and it was higher in the subsurface than in the surface layers. The total Cr content in the subsurface upland soil U3 of group II was higher than in other upland soils of group I, and no large differences were observed between paddy soils of groups I and II (Fig. 3a). The median values of total Cr contents in the surface and subsurface layers of all three types of fields were 86.1 and 72.8 mg kg^{-1} , respectively (Fig. 3b). The contents of Cr in both layers of the forest field F3 and the subsurface layer of the upland field U3 were identified as upper outliers (Fig. 3b). The contents of HCl-extractable Cr were negligible in all types of soils (Fig. 3a).

Table 2 Sequential extraction scheme for heavy metals

Fractions	Reagents	Soil/ Soln. ratio	Condition	Chemical forms of heavy metals
Water-soluble (Ws)	Deionized water	1:5	Shake 1 h	Water-soluble
Exchangeable (Ex)	1.0 mol L ⁻¹ CH ₃ COONH ₄ (pH 7.0)	1:10	Shake 2 h	Exchangeable
Acid-soluble (Aci)	25 g L ⁻¹ CH ₃ COOH (pH 2.6)	1:10	Shake 6 h	Acid-soluble
Mn oxide-occluded (MnO)	0.1 mol L ⁻¹ NH ₂ OH.HCl (pH 2.0)	1:50	Shake 0.5 h	Specifically adsorbed heavy metals by Mn oxide
Organically bound (OM)	0.1 mol L ⁻¹ Na ₄ P ₂ O ₇ (pH 10.0)	1:50	Shake 24 h	Occluded by organic matter
Fe oxide-occluded (FeO)	0.175 mol L ⁻¹ (NH ₄) ₂ C ₂ O ₄ , 0.1 mol L ⁻¹ H ₂ C ₂ O ₄ , 0.1 mol L ⁻¹ ascorbic acid (pH 3.1)	1:50	Shake 4 h, then stir occasionally in boiling water for 0.5 h	Specifically adsorbed heavy metals by Fe oxide
Residual (Res)	5 mL conc. HClO ₄ , 10 mL conc. HNO ₃ , 15 mL conc. HF			Occupied in crystal lattice of minerals

Iwasaki et al. (1997), with some modification

Copper The total Cu contents in both layers of the forest field (F3) of group II were higher than those of group I soils (Fig. 4a). In addition, the total Cu content in the subsurface upland soil U3 of group II was higher than in other upland soils of group I, and it was 2.8 times higher than in the surface soil U3 (Fig. 4a). For paddy soils, the total content of Cu in the surface layer of paddy field P18 of group II was particularly 3.8 times higher than in the subsurface layer (Fig. 4a). The same median values of 45.7 mg kg⁻¹ were found for surface and subsurface soils of all types of fields (Fig. 4b). Total Cu content of the surface and subsurface layers of forest field F3, the subsurface layer of the upland field U3, and the surface layer of the paddy field P18 were identified as upper outliers.

Lead Generally, for forest and upland soils, no significant differences were observed between groups I and II (Fig. 5a). The most pronounced gradient at one location, almost five times higher in the surface than in the subsurface layer, was detected at site P18 of group II (Fig. 5a). The median values of total Pb contents in the surface and subsurface layers of all three types of fields were 48.7 and 42.7 mg kg⁻¹, respectively (Fig. 5b). The surface layer of paddy field P18 was indicated as an upper outlier in the box plot of total Pb content (Fig. 5b).

Zinc The most pronounced gradients, from 1.5 to 2 times higher in the surface layer compared to the subsurface layer, were detected in the paddy fields P10, P18, and P21 of group II (Fig. 6a). Except for

Table 3 Physicochemical properties of the studied soils

	pH (H ₂ O)	Exchangeable				CEC	TC (g kg ⁻¹)	Clay (%)
		Ca (cmol(+)kg ⁻¹)	Mg	K	Na			
Forest (n=4)	5.0±0.3	0.45±0.59	0.07±0.08	0.11±0.07	0.05±0.02	5.5±1.4	10.7±6.5	36.3±10.5
Paddy (n=36)	7.3±0.8	13.7±7.24	0.05±0.02	0.21±0.09	0.62±0.47	9.7±3.1	13.7±7.2	27.6±9.8
Upland (n=12)	7.9±0.5	17.3±8.51	0.34±1.10	0.14±0.06	0.72±0.47	7.1±3.1	7.0±4.9	12.0±7.2

Table 4 Ranges, means, and median values of total and HCl-extractable contents of heavy metals in the soils sampled

Depth (cm)	Total (mg kg ⁻¹)							HCl-extractable (mg kg ⁻¹)							
	Cd	Cr	Cu	Pb	Zn	Cd	Cr	Cu	Pb	Zn	Cd	Cr	Cu	Pb	Zn
Grouped by land use															
Forest (n=4)	0–5	Mean	0.12	271	73.5	19.8	61.6	<dl	0.09	2.7	2.23	1.72			
		Range	<dl–0.24	117–424	38.4–109	19.1–20.4	44.5–78.7	<dl	0.03–0.15	1.44–3.97	1.74–2.71	1.50–1.93			
20–25		Mean	<dl	379	95.2	13.2	75.5	<dl	0.08	2.94	2.04	0.51			
		Range	<dl	142–616	74.1–116	3.68–22.8	72.1–78.8	<dl	<dl–0.14	1.92–3.96	1.37–2.70	0.35–0.67			
Paddy (n=36)	0–5	Mean	0.46	84.1	52.9	67.8	159	0.24	0.60	14.4	15.9	29.0			
		Range	<dl–1.28	23.0–136	19.6–193	25.2–340	47.3–381	<dl–0.75	<dl–3.27	0.99–101	0.50–169	1.85–153			
20–25		Mean	0.23	73.7	41.3	44.7	118	0.15	0.40	7.54	5.04	11.6			
		Range	<dl–0.58	16.8–107	13.5–63.2	25.6–65.1	22.8–186	<dl–0.32	<dl–1.61	0.59–21.8	0.92–13.9	0.37–36.4			
Upland (n=12)	0–5	Mean	0.15	92.6	50.4	50.7	104	0.14	<dl	2.33	1.78	4.18			
		Range	<dl–0.30	72.7–128	30.8–64.7	30.4–80.4	80.2–131	<dl–0.19	<dl–0.30	<dl–4.93	<dl–5.38	1.47–6.23			
20–25		Mean	0.15	85.4	65.1	55.5	95.3	<dl	<dl	2.49	1.25	3.01			
		Range	<dl–0.40	44.8–190	19.6–157	33.0–76.2	53.2–144	<dl–0.2	<dl–0.17	6.87–14.9	<dl–3.20	0.26–5.99			
Grouped by potential contamination source															
Group I	0–5	Mean	0.17	88.2	45.3	52.1	108	0.08	0.13	3.16	3.25	4.84			
		Range	<dl–0.42	72.7–118	30.8–64.7	19.1–80.4	44.5–156	<dl–0.23	<dl–0.32	<dl–7.52	<dl–11.0	1.93–6.23			
20–25		Mean	0.12	81.2	45.1	46.9	101	0.06	0.13	3.16	2.33	3.58			
		Range	<dl–0.29	44.9–143	19.6–74.1	22.8–76.2	53.2–129	<dl–0.20	<dl–0.39	<dl–6.87	<dl–6.96	0.67–5.99			
Group II	0–5	Mean	0.47	107	58.5	64.5	155	0.22	0.61	14.7	16.0	24			
		Range	<dl–1.28	23.0–424	19.6–193	20.4–340	47.4–381	<dl–0.75	<dl–3.27	0.25–101	0.32–169	1.47–153			
20–25		Mean	0.23	110	54.1	43.7	114	0.12	0.40	7.54	4.78	11.5			
		Range	<dl–0.58	16.8–616	13.5–157	3.68–73.0	22.8–186	<dl–0.30	<dl–1.61	0.59–21.8	0.44–37.4	0.26–36.4			

Group I: purely agricultural soil; group II: agricultural soil near contamination sources; <dl: below detection limit of Cd (0.05 mg kg⁻¹ for total Cd content; 0.005 mg kg⁻¹ for HCl-extractable metal content)

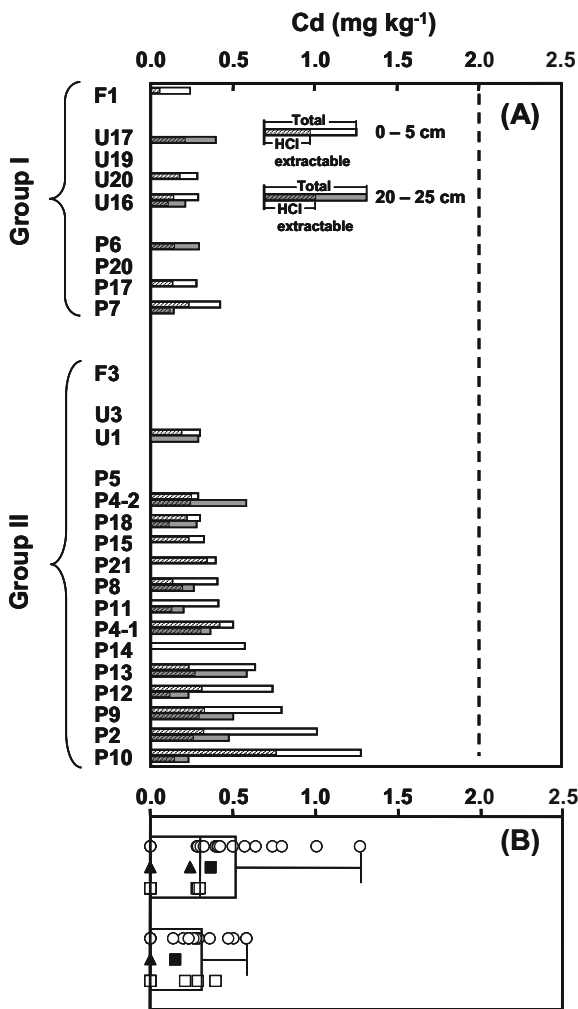


Fig. 2 **a** Total and HCl-extractable Cd in the soils. For each sampling site, *white* and *gray* bars indicate the surface (0–5 cm) and subsurface (20–25 cm) soil layer, respectively. The *hatched* part of each bar indicates the amounts of Cd extracted by 0.1 mol L⁻¹ HCl. The *vertical line* shows the maximum allowable limit of Cd content for Vietnamese agricultural soils (2 mg kg⁻¹). **b** Box plot of total Cd contents. *Left* and *right* edges of a box indicate the lower and upper quartiles, respectively; the *line inside the box* shows the median. *Horizontal lines protruding from the box (whiskers)* indicate the 25th and 75th percentiles. Forest soils (*triangle*), paddy soils (*circle*), upland soils (*open square*), mean values (*filled square*)

these cases, the differences between group I and II of forest or upland fields were insignificant (Fig. 6a). The median values of total Zn contents in the surface and subsurface layers of all field types were 124 and 116 mg kg⁻¹, respectively (Fig. 6b). The surface layers of paddy fields P10, P18, and P21 contained

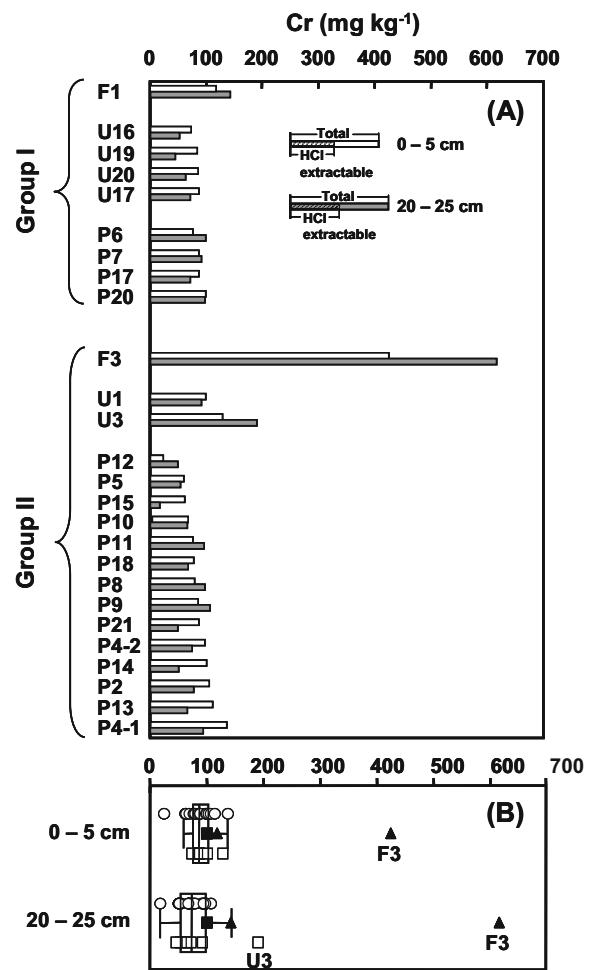


Fig. 3 **a** Total and HCl-extractable Cr in the soils. Total and HCl-extractable Cr in the soils. For each sampling site, *white* and *gray* bars indicate the surface (0–5 cm) and subsurface (20–25 cm) soil layer, respectively. The *hatched* part of each bar indicates the amounts of Cr extracted by 0.1 mol L⁻¹ HCl. **b** Box plot of total Cr contents. Further details as in Fig. 1

significantly higher total contents of Zn than any other samples, as indicated by the upper outliers in the box plot (Fig. 6b).

3.2 Sequential Extraction of Heavy Metals in Selected Samples

In order to characterize the forms of heavy metals and their mobility in the soils, sequential extraction was carried out for selected samples (Fig. 7). The surface and subsurface layers of a soil with low Cu, Pb, and

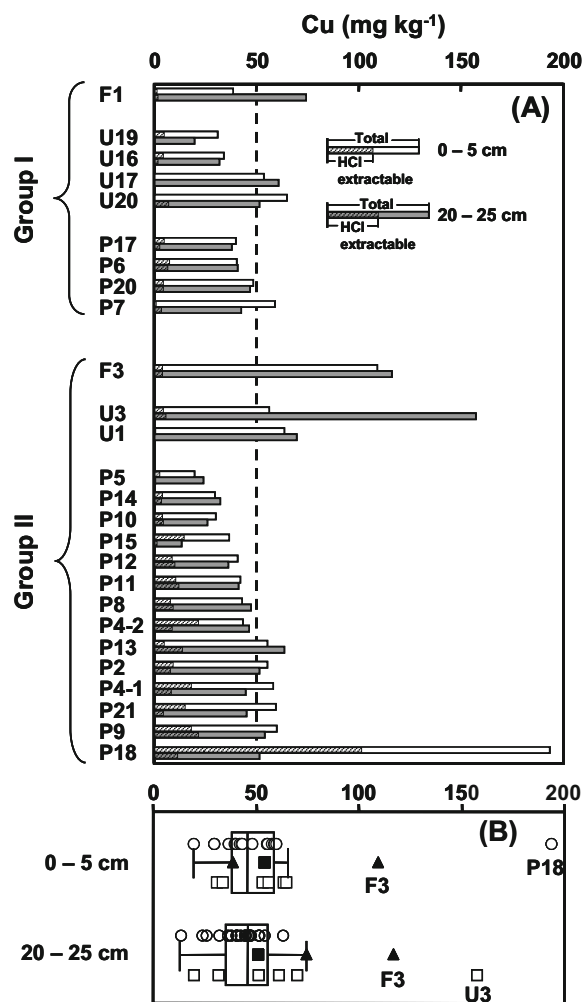


Fig. 4 a Total and HCl-extractable Cu in the soils. Total and HCl-extractable Cu in the soils. For each sampling site, *white* and *gray bars* indicate the surface (0–5 cm) and subsurface (20–25 cm) soil layer, respectively. The *hatched part of each bar* indicates the amounts of Cu extracted by 0.1 mol L⁻¹ HCl. **b** Box plot of total Cu contents. The *vertical line* shows the maximum allowable limit of Cu content for Vietnamese agricultural soils (50 mg kg⁻¹). Further details as in Fig. 1

Zn contents (P5) and the outliers in the box plots that contain elevated levels of Cu, Pb, Zn (P18), Zn (P10, P21), and Cu and Cr (F3, U3) were selected. According to the Vietnamese soil map, the forest field F3 is located in an area dominated by Ferrasols; upland field U3 is located nearby and also close to the river. Therefore, it was interesting to clarify the chemical forms of Cr and Cu which were present at relatively high levels in the soils from F3 and U3 sites. Because of the low level of

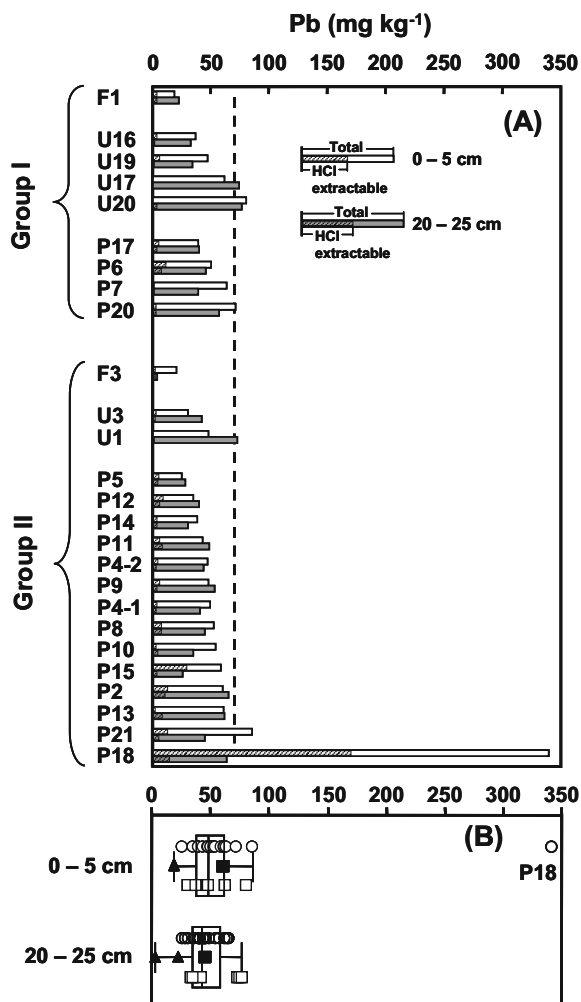


Fig. 5 a Total and HCl-extractable Pb in the soils. Total and HCl-extractable Pb in the soils. For each sampling site, *white* and *gray bars* indicate the surface (0–5 cm) and subsurface (20–25 cm) soil layer, respectively. The *hatched part of each bar* indicates the amounts of Pb extracted by 0.1 mol L⁻¹ HCl. **b** Box plot of total Pb contents. The *vertical line* shows the maximum allowable limit of Pb content for Vietnamese agricultural soils (70 mg kg⁻¹). Further details as in Fig. 1

Cd in the sampled soils, the extraction results for Cd are not discussed. The recovery ratios of heavy metals, calculated by division of the sum of the contents in each fraction by the total content, varied from 89.7% to 114% in the selected soils.

Chromium Generally, similar distribution patterns of Cr were observed in the surface and subsurface layers of the forest site F3 and the upland site U3. For both

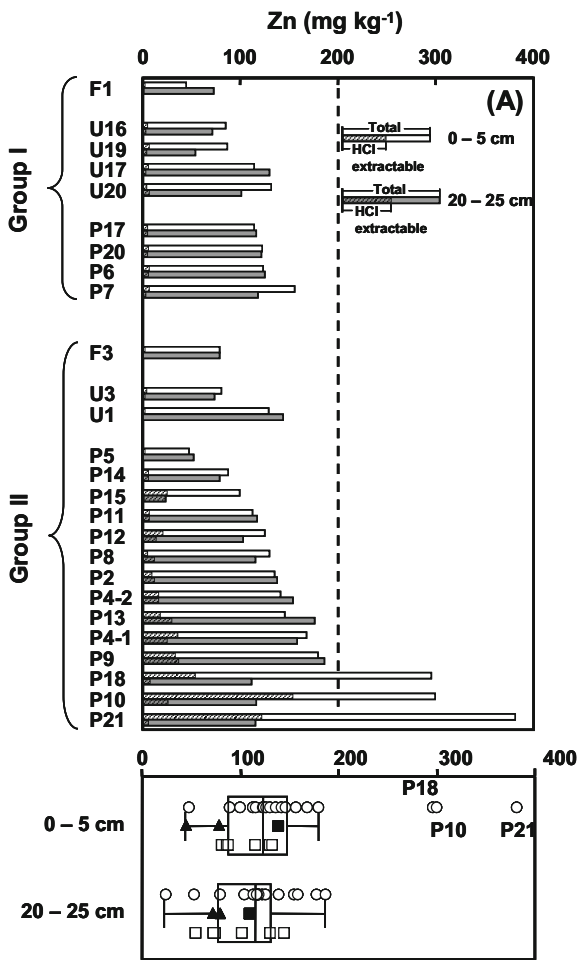


Fig. 6 **a** Total and HCl-extractable Zn in the soils. Total and HCl-extractable Zn in the soils. For each sampling site, *white* and *gray bars* indicate the surface (0–5 cm) and subsurface (20–25 cm) soil layer, respectively. The *hatched part of each bar* indicates the amounts of Zn extracted by 0.1 mol L⁻¹ HCl. **b** Box plot of total Zn contents. The *vertical line* shows the maximum allowable limit of Zn content for Vietnamese agricultural soils (200 mg kg⁻¹). Further details as in Fig. 1

soil layers of the F3 field, more than 90% of the Cr content distributed into the FeO and Res fractions (Fig. 7a). In addition, 1.1% and 2.9% were detected in the OM fraction of the surface and subsurface layers, respectively, of F3. The subsurface layer from F3 contained a higher proportion of Cr in the Res fraction compared to the surface layer. In both soil layers from U3, Cr primarily existed in Res fraction (about 80%), while smaller amounts (about 20%) were extracted in the FeO fraction. The other fractions contained negligible Cr (Fig. 7a).

Copper The distribution pattern of Cu was similar in the surface and subsurface layers of the forest site F3 and the upland site U3. In the surface and subsurface layers of F3, about 90% of Cu belonged to the FeO and Res fractions (Fig. 7b). The smaller proportions of 10.4% and 5.9% were found in the OM fraction of the surface and subsurface soils, respectively (Fig. 7b). In the subsurface layer of F3, 2.5% of the Cu was detected in the MnO fraction, while the corresponding amount in the surface layer was negligible. In both layers of the upland soil U3, Cu was dominant in the FeO fraction (>50%), followed by the Res fraction (about 30%); less than 10% of Cu was found in the OM and MnO fractions (Fig. 7b). The proportions of Cu in the MnO fraction extracted from the surface and subsurface layers of the upland soil U3 were higher than in the equivalent layers of the forest soil F3 (Fig. 7b).

In the low-Cu soil of P5, 63–97% of Cu distributed to the Res and FeO fractions in the surface and subsurface layers. In the surface layer, 20.2% and 10.7% of Cu were found in the OM and MnO fractions, respectively, and only about 3% of Cu was detected in the Aci and Ex fractions. In the subsurface layer, Cu was not found in significant proportions in these fractions (<2%; Fig. 7b). On the other hand, the surface layer of P18, which had a high total Cu content, showed significantly larger proportions of Cu (11.5% and 3.7%) in the Aci and Ex fractions than the surface layer of P5. In comparison to the surface layer of P18, the subsurface layer of this site contained lower proportions of Cu (<4%) in the Aci and Ex fractions (Fig. 7b).

Lead In the surface and subsurface layers of the low-Pb soil of P5, Pb was mainly extracted in the Res, FeO, and MnO fractions (Fig. 7c). In contrast, in the surface layer of P18, only 7.78% of Pb was retained in the Res fraction. In addition, the surface layer of P18 showed significant proportions of Pb in the OM, Aci, and Ex fractions (20%, 7.0%, and 3.1%, respectively), while in the subsurface layer of P18, only 3.9% of Pb was extracted in the Aci fraction, and the proportion of Pb in OM and Ex fractions was negligible (Fig. 7c).

Zinc In both layers of the low-Zn soil P5, more than 90% of the total Zn content was present in the Res and FeO fractions. Around 6% of Zn existed in

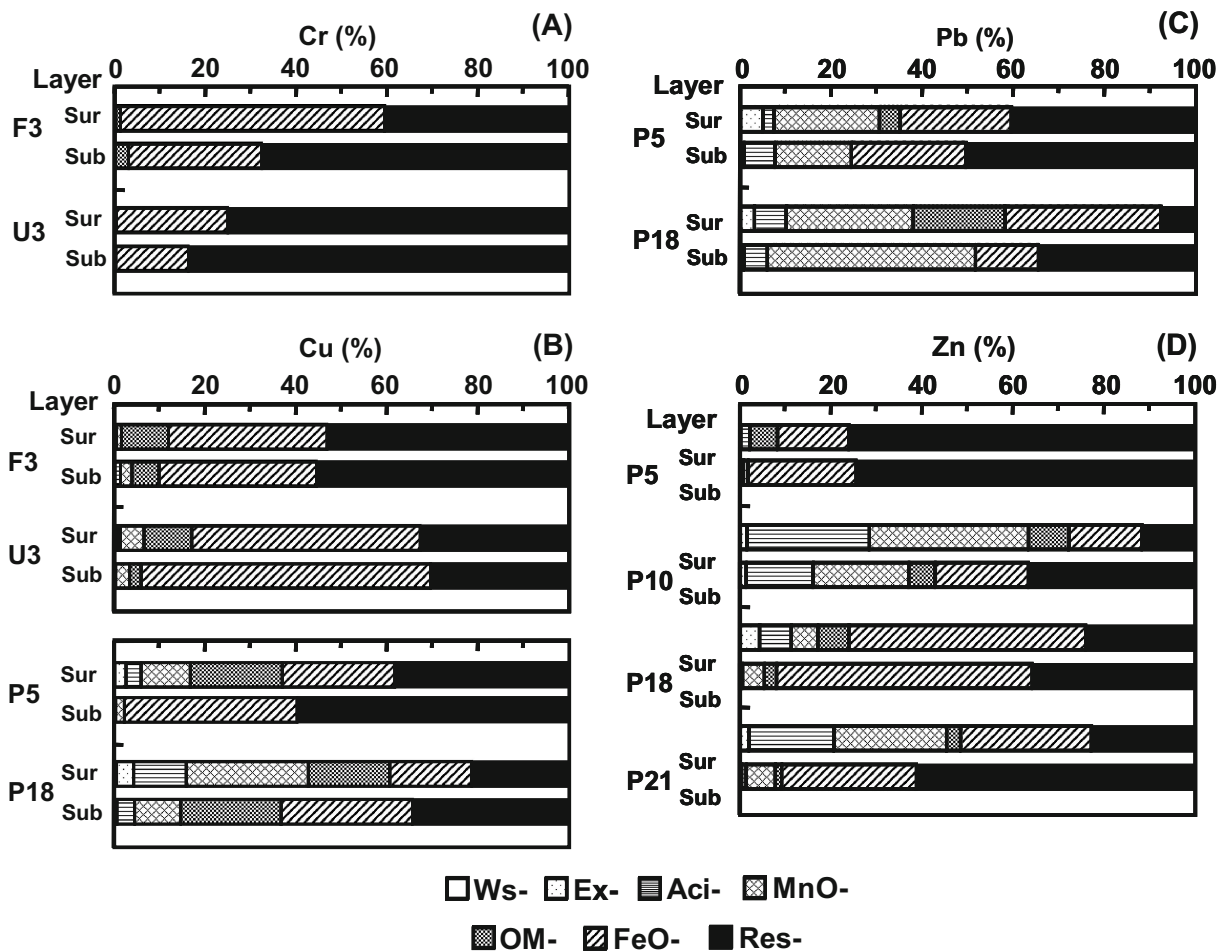


Fig. 7 Heavy metal contents of selected soils divided into seven chemical fractions. **a** Cr, **b** Cu, **c** Pb, **d** Zn. Extraction steps: *Ws*: water-soluble fraction, *Ex* Exchangeable fraction, *Aci*

acid-soluble fraction, *MnO* specifically adsorbed by Mn oxide fraction, *OM* occluded by organic matter fraction, *FeO* specifically adsorbed by Fe oxide fraction, *Res* residual fraction

the OM fraction of the surface layer of P5; other fractions were insignificant (<2%; Fig. 7d). In contrast, significantly reduced proportions (11.7–61%) of Zn in the Res fraction were observed in both layers of the soils from P10, P18, and P21. In the surface layers of these three sites, more than 75% of Zn occurred in the non-residual fractions. Of Zn, 7.1–26.8% and 5.7–34.7% were observed in the Aci and MnO fractions, respectively. Lower proportions from 3.0% to 9.0% were detected also in the OM fraction, and <5% of Zn was extracted from Ex fractions (Fig. 7d).

4 Discussion

An accumulation of high levels of Cu (193 mg kg^{-1}), Pb (340 mg kg^{-1}), and Zn (381 mg kg^{-1}) was observed in the surface layer of paddy field P18. The high Cu content in this soil was probably caused by smelting activities in the traditional copper casting village. Smelting scraps at high temperature and polishing of the final products possibly introduce a hazard to the surrounding soil environment through wastewater leaching or atmospheric deposition. Lead recycling from batteries in a neighbor village might

introduce Pb to the soil through atmospheric deposition (Le 2002). According to Le (2002), 46.4 and 26.2 mg/m³ of Pb were detected in gas emissions at 10 and 30 m, respectively, from the melting oven. Zn may occur together with Cu in bronze and brass or with Pb in batteries (Siegel 2002). Thus, the industrial activities might result in point pollution with Cu, Pb, and Zn. This is consistent with high accumulations of heavy metals observed in the topsoil surrounding metal smelters in many countries (Alloway 1990; Kaasalainen and Yli-Halla 2003). Compared to the subsurface soil of P18 as well as both soil layers at P5, Cu, Pb, and Zn in the surface soil of P18 tend to distribute in more mobile fractions, particularly in Ex, Aci, MnO, and OM fractions, suggesting an anthropogenic input of metals into the surface layer of the paddy field P18 (Karczewska 1996). The results of Cu and Pb fractionation in the surface soil of P18 were in line with data by Kaasalainen and Yli-Halla (2003) and Li et al. (2007). Kaasalainen and Yli-Halla (2003) fractionated Cu and Pb in agricultural soils and found that 49–72% of Cu occurred in the exchangeable and specifically adsorbed fraction and in the Fe and Mn (hydr)oxide-bound fractions; Pb was mostly adsorbed by Fe and Mn (hydr)oxides. Consistently, Pb in paddy soils was primarily adsorbed to organic matter and Fe–Mn oxides and also occurred in the residual fraction (Li et al. 2007).

Furthermore, elevated levels of Zn in the surface layers of the paddy fields P10 (299 mg kg⁻¹) and P21 (381 mg kg⁻¹) were found. P10 is located close to a phosphorous fertilizer factory. In addition, there is a battery factory about 200 m from the phosphorous fertilizer factory. P21 is located in the vicinity of an industrial zone. Therefore, wastewaters from nearby factories, which are discharged into irrigation water channels, may be one of the main reasons for the high Zn contents in the surface soils of P10 and P21. N–P–K fertilizers, which often include traces of Zn, Cu, B, Mo, Co, etc., are widely applied in Vietnam. The dosage of N–P–K (6:11:2) fertilizer commonly applied in the Red River Delta is about 500 kg ha⁻¹. Such an intensive application is quite possibly another factor contributing to the high Zn levels in the soils. In comparison to other soils, relatively high proportions of total Zn (51% and 32%) were extracted by 0.1 mol L⁻¹ HCl from the surface layers of P10 and

P21, suggesting a high Zn mobility in these soils. The visually detectable proportions of Zn in the Ex fraction (1.69% and 2.12%) and the high proportions in the Aci fraction (26.8% and 18.6%) in the surface layers of P10 and P21 indicated that Zn was more readily mobile in these soil layers than in the subsurface layer and in both layers of P5. Similar results were documented by Adriano (2001b). We conclude that sites P10 and P21 can be considered locations of probable point pollutions.

In addition, elevated contents of Cu and Cr were detected in the subsurface layer of upland field U3 and in both horizons of the forest field F3 (outliers in Fig. 3b). U3 is located near Da River and close to the forest site F3. The map of Vietnamese mineral distribution (2000) indicates that pyrite- and copper-containing minerals are abundant in the geological basis of site F3. At this site, soil from 40- to 45-cm depth was also collected and analyzed (data not shown). The results indicated that Cr and Cu contents gradually increased with depth (from 424 to 750 for Cr and from 108 to 130 for Cu), suggesting a lithogenic origin of the two elements at this site. Cr and Cu in the soils of F3 and U3 were strongly incorporated into the Fe oxides (FeO) and mineral structure (Res), resulting in low mobility of the two metals in these soils. A low mobility of Cr was reported also under high soil pH (8.1–9.1; Luchon-Constantino et al. 2005). Instead of strong adsorption by Fe oxides like in the forest field F3, Cr in the upland field U3 was more strongly incorporated in the crystalline lattice of minerals. Furthermore, a larger proportion of Cu was adsorbed to Mn oxide in the upland field U3 than in the forest field F3. The results appear in line with the report by Iwasaki et al. (1997) in which the Res, FeO, and OM fractions of Cu were the most important ones in forest soils, while in agricultural soils, the adsorption of Cu by Mn oxides was also significant. Consequently, the accumulation of Cr and Cu in the forest site F3 and the upland site U3 was presumed to be related to the pedogenic substrate, and therefore, the sites could be considered natural point sources of pollution (Adriano 2001a).

Generally, 31%, 63%, 79%, 77%, and 71% of the sampled soils exceeded the average levels of Cd (0.35 mg kg⁻¹), Cr (70 mg kg⁻¹), Cu (30 mg kg⁻¹), Pb (35 mg kg⁻¹), and Zn (90 mg kg⁻¹), respectively,

found in soils around the world (Bowen 1979). In the forest soils, the median value of total Cu (91.4 mg kg^{-1}) was significantly higher than the average Cu content in ferralsols reported by Tran and Tran (2002). In contrast, the median values of the total Cr, Pb, and Zn contents in the forest soils were comparable to the average values reported for these metals (2.36, 8.20, and 92.5 mg kg^{-1} , respectively) in Vietnamese ferralsols (Tran and Tran 2002). The low total contents of Cd in the forest soils ($<0.05\text{--}0.12 \text{ mg kg}^{-1}$) were compatible with the ranges (<0.01 to 0.08 mg kg^{-1}) in ferralsols documented by Ho and Egashira (2001). The surface layers of paddy fields that were analyzed exceeded the maximum allowable limit in Vietnamese agricultural soils for Cu (50 mg kg^{-1}) in 39%, for Pb (70 mg kg^{-1}) in 17%, and for Zn (200 mg kg^{-1}) in 17% of all cases. For the subsurface layers of paddy field soils, only Cu content in 22% of all samples was found exceeding the allowable limit. In upland field soils, the total contents of Cu and Pb were higher than the limits in 67% and 17%, respectively, of the surface layers and in 67% and 50%, respectively, of the subsurface layers. Paddy and upland soils showed higher total Cd contents ($<0.05\text{--}1.28 \text{ mg kg}^{-1}$) than previously reported ($0.05\text{--}0.09$; Ho and Egashira 2001). However, the total contents of Cd in paddy and upland field soils were lower than the maximum allowable limit for Vietnamese agricultural soils (2 mg kg^{-1}). Unfortunately, the limit for Cr of agricultural soil in Vietnam is unavailable. Taken together, our results indicated an enrichment of Cu, Pb, and Zn in the surface layers of paddy field soils and of Cu and Pb in the surface layers of upland field soils.

On the other hand, the significantly higher total Cd contents in the surface layers of group II as compared to group I suggested emission of Cd from external sources. However, the level of Cd in these soils was still below the allowable limit. Although differences in total metal contents between groups I and II were found only in the case of Cd, differences in HCl-extractable content between those two groups were observed in several metals, implying higher metal mobility in the soils of group II. In comparison to group I, Cd, Cr, and Zn were more mobile in the surface soils of group II, and so were Cr, Cu, Pb, and Zn in the subsurface soils of group II. The enhanced metal mobility in soils at locations close to potential contamination sources, hence, may increase the stress level for plants. Therefore, not only point

pollutions but also other potential contamination sources should be taken into account as well.

The contents of those metals in the soils from the Red River Delta were compatible with results from agricultural soils influenced by accelerated industrialization and urbanization in China in recent years (Huang et al. 2007; Khan et al. 2008; Zhao et al. 2007). In addition, relatively similar results with respect to metal fractions extractable by 0.1 mol L^{-1} HCl were reported from agricultural soils (Takijima and Katsumi 1973; Yanai et al. 1998).

5 Conclusions

Although no serious large-scale heavy metal pollution was found in the Red River Delta, the influence of industrial activities in industrial zones and traditional handicraft villages on the levels and mobility of heavy metals in the soils from group II (close to potential contamination source) was recognized. In addition, several point pollutions were identified in this study. Natural point pollutions with Cr and Cu were observed in a forest field and the vicinal upland field where levels of Cr and Cu are assumed to be enriched by the pedogenic process. Anthropogenic point pollutions possibly caused by industrial activities were found in several paddy fields. High accumulations of Cu, Pb, and Zn were observed in the surface soil of site P18 which was neighbored by two handicraft villages with copper casting and lead recycling activities. In addition, elevated amounts of Zn were also detected in the surface layers of P10 and P21, probably resulting from activities in the industrial zones in the south of Hanoi and in Hungyen, respectively. In the surface layer of these soils, larger proportions of Cu, Pb, and Zn distributed in the Ex and Aci fractions compared to the low metal soil P5 suggested higher metal solubility at these sites. Results of HCl-extractable heavy metal analyses and of sequential extraction indicated that the anthropogenic point pollutions should be of serious concern since they pose direct risks to staple crops and consequently to the human health. Considering the rapid industrial development in Vietnam, there is little reason for optimism unless proper management systems for manufacturing activities in traditional handicraft villages and industrial zones, as well as effective removal techniques for contaminants, have been established.

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