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Two surface soil samples were collected from each of alluvial soils and grey degraded soils in Hanoi City, Vietnam and subjected to soil chemical and physical analyses and to a batch adsorption test for evaluation of the adsorption capacity of heavy metals such as Cu, Pb, Zn and Cd. The results showed that the alluvial soil had the high organic matter, free iron oxides, clay and active 2:1–type silicate minerals contents, and high pH value in comparison with those of the grey degraded soil. The adsorption isotherm of heavy metals by the soils was well fitted to the Freudlich model. The adsorbents for heavy metals as a total of organic matter, free iron oxides, and clay minerals in terms of both amount (clay content) and type (clay mineralogical composition) were larger for the alluvial soil than for the grey degraded soil. As a result, the adsorption capacity of heavy metals was distinctly higher for the former than for the latter. Within a soil, the adsorption capacity was decreased in the sequence of Pb   Cu   Zn for the alluvial soil and of Pb   Zn   Cu for the grey degraded soil.

INTRODUCTION

Hanoi is one of the biggest and most advanced cities in Vietnam. The rapid industrialization and motorization throughout the city, and the intensive cultivation in the sub–urban areas, in the positive side, have contributed largely to the regional or national socio–economic development. On the other hand, those have put the city under severe environmental problems including soil pollution by heavy metals. Nguyen (2006) stated that soils from industrial zones of Donganh, Gialam and Socson Districts (Hanoi suburb) were polluted by heavy metals due to discharge of untreated wastes from nearby factories. In some areas, accumulation of heavy metals in agricultural soils was considered as a consequence of application of large amounts of chemical fertilizers, agricultural chemicals and organic amendments (Nguyen and Duong, 2004; Ha and Pham, 2005). Ho and Egashira (2000) reported that sediments of the rivers flowing through industrialized and densely–populated areas of Hanoi City were polluted with various heavy metals. They mentioned that heavy metals might be accumulated in agricultural soils by applying those river/canal sediments as an organic fertilizer to keep soil fertile. Nguyen *et al.* (2006) predicted that under the accumulation rate as recorded recently, the heavy metal concentration in soils of Hanoi City would reach the maximum allowable level of the Vietnamese standard within next few decades.

Concerning the accumulation of heavy metals, adsorption is considered a major process or a most important mechanism for controlling the metal concentration in soil. Heavy metals are bound to various soil components, of which the most important ones are organic matter, free iron oxides, and clay minerals. Therefore, different soils would have different adsorption capacities of a heavy metal. The main soil types in Hanoi City are alluvial soils and grey degraded soils which are normally found in an associated distribution with each other (Fig. 1). In reference to alluvial soils, the fertility of grey degraded soils has been recognized to decline in terms of chemical and physical properties (VSSS, 1996; NISF and DSTPQ, MARD, 2002) and clay mineralogy (Do *et al.*, 2002; Nguyen *et al.*, 2006). Accompanied with the soil fertility decline, adsorption capacity of heavy metals would be expected to be decreased in grey degraded soils. If this is the case, heavy metals are hardly accumulated and held in soil but are leached away to groundwater in the grey degraded soil area, leading to the spread of heavy metals to the environment which would raise difficulties for remediation after pollution.

The purposes of the present study are: (1) to compare the adsorption capacity of heavy metals between alluvial soils and grey degraded soils in Hanoi, Vietnam; and (2) to characterize the adsorption capacity of heavy metals of the soils in relation to heavy metal attributes and composition of adsorbing soil components.

MATERIALS AND METHODS

Soil samples and sampling locations

Figure 1 shows locations of sampling sites on the soil map of Vietnam. The mapped area covers the entire Hanoi City. The main soil types shown in the map are alluvial soils of the Red River system composed of sediments from the Red River and the upper stream of the

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Duong River, grey degraded soils derived from old alluvium of the Red River system, and ferralitic soils. One surface soil sample representing alluvial soils of the Red River system was collected in Minhkhai Commune, Tuliem District and another surface soil sample representing grey degraded soils was collected in Phuminh Commune, Socson District. Both soil types have been used as paddy and recently subjected to cultivation of cash crops or rice–cash crops.

Soil samples were taken at a depth of 0 to 15 cm, air–dried and gently ground to pass through a 2–mm sieve, before export to Japan. Chemical, physical and mineralogical properties of the soils and adsorption of heavy metals by them were examined in Kyushu University, Japan.

Procedures for chemical, physical and mineralogical analyses

The pH (H_2O) was measured in the suspension having a soil/water ratio of 1/2.5 by a pH meter. Organic carbon was measured by the dry combustion method using a total organic carbon analyzer and multiplied by the coefficient of 1.724 to give the organic matter content. Free iron oxides were digested by shaking with sodium hydrosulfite powder and citrate solution (Egashira *et al.*, 2002) and the concentration of iron in the digest was determined by an atomic absorption spectrophotometer.

In the particle–size analysis, organic matter was first removed by treatment with hot 7% H_2O_2. The sample was then dispersed by an ultrasonic vibration, and adjusted to the pH 10 by addition of appropriate amounts of 1 M NaOH. The whole $2\,\mu m$ clay fraction was separated by repeated sonification–sedimentation–siphoning with an intermittent pH adjustment. The whole 2–$20\,\mu m$ silt fraction was separated by repeated sedimentation and siphoning, followed by separation of the 20–200 and 200–2,000 μm sand fractions by wet–sieving. After oven–drying at $105\,°C$, each fraction was weighed to calculate the particle–size distribution of a soil.

The $2\,\mu m$ clay fraction separated in the particle–size analysis was used to determine the clay mineralogical composition by the X–ray diffraction (XRD) method (Do *et al.*, 2002; Nguyen and Egashira, 2005b). Parallel–oriented samples saturated with Mg and K were prepared and analyzed by a Rigaku X–ray diffractometer after air–drying and glycerol–solvation for the Mg–saturated clay, and after air–drying and heating at $300\,°C$ and $550\,°C$ for the K–saturated clay. Relative mineral contents in the clay fraction were semi–quantitatively estimated on the basis of the XRD peak intensities. The relative proportions of the minerals of a sample were normalized to 100% under assumption of the same pro-
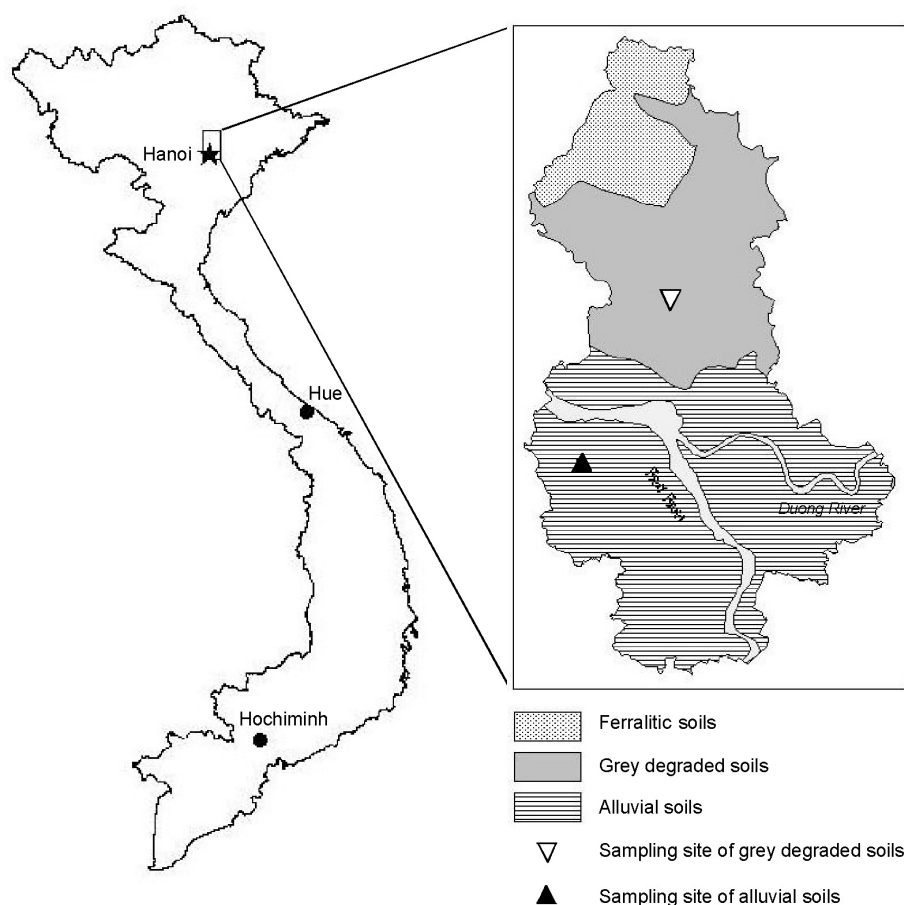

Fig. 1. Locations of sampling sites on the soil map of Vietnam.

portionality between the peak intensity and the content for each mineral.

Batch adsorption test

The batch equilibrium test was used for determination of the heavy metal adsorption isotherm of a soil. Seven concentration levels of Cu, Pb and Zn at 50, 100, 250, 500, 1000, 1500 and 2000 mg/L, and 6 concentration levels of Cd at 5, 10, 20, 50, 70 and 100 mg/L were prepared from the respective metal nitrate salts. Seven or six sets of 2.00 g air–dry soil were exactly weighed into a 50–mL centrifuge tube and mixed with 20 mL of each of the above heavy metal solutions. The mixture was shaken for 24 h at room temperature of 25 °C for equilibration and then centrifuged at 2,000 rpm for 15 min to separate the supernatant solution from soil. The equilibrium metal concentration in solution was determined by an atomic absorption spectrophotometer. The experiment was done in duplicate to ensure the accuracy of determination.

The amount of heavy metal adsorbed was calculated by the equation:

$$q_a = \frac{(C_i - C_f)\,V}{m}$$

where q_a is the amount of metal adsorbed per unit mass of soil (mg/kg); C_i is the initial concentration (mg/L) of the metal nitrate solution before batch test; C_f is the equilibrium (final) metal concentration (mg/L) in solution after batch test; V is the volume of the metal nitrate solution (mL); and m is the mass of soil (g) used in the batch test.

The calculated q_a values were large. Therefore, in the present study, we divided left– and right–hand sides of the equation by 10 for a better datum exhibition. Because the ratio of V to m was 10:1, the above equation can be written in a simpler form:

$$q_a 10^{-1} = C_i - C_f$$

RESULTS AND DISCUSSION

Some chemical and physical properties of the soils

The pH, organic matter and free iron oxides contents, particle–size distribution and texture of the alluvial soil and grey degraded soil are given in Table 1. The alluvial soil had a slightly alkaline reaction (pH 7.7), medium organic matter content (17.2 g/kg), high free iron oxides content (43.3 g/kg), and a texture of clay loam with the clay, silt, fine sand and coarse sand contents of 17.2, 27.5, 54.5 and 0.8%, respectively. Those properties have been well characterized for Eutric Fluvisols of the Red River system as reported by Nguyen *et al.* (2005) and Nguyen and Egashira (2005a). For the grey degraded soil, the pH value (5.7) was in an acid range and the organic matter content (13.8 g/kg) was lower than that of the alluvial soil. Especially, the free iron oxides content (4.3 g/kg) was very low resulting in the grey color, a morphological characteristic of grey degraded soils. Another characteristic of the grey degraded soil was a coarse surface texture of sandy loam with the low clay (6.7%) and silt (15.7%) contents and the high fine sand (74.1%) content. This is considered a corollary of soil degradation (NISF and DSTPQ, MARD, 2002).

Clay mineralogy of the soils

The relative mineral contents in the $< 2\,\mu$m clay fraction of the alluvial soil and grey degraded soil are shown in Table 2. Mica (40%) and kaolinite (24%) were predominant clay minerals of the alluvial soil accompanied with minor amounts of chlorite (8%), vermiculite (12%) and smectite (2%). Minerals other than layer silicate minerals such as goethite, gibbsite, quartz and feldspars were detected with a range from trace to less than 10% in the clay fraction. The clay mineral composition of the alluvial soil in the present study was in accordance with that of alluvial soils from the Red River system in reference to the previous study (Nguyen and Egashira, 2005b).

The grey degraded soil had the lower mica (14%) and chlorite (3%) while higher kaolinite (36%) contents

Table 1. The pH, organic matter and free iron oxides contents, particle–size distribution and texture of the alluvial soil and grey degraded soil

| Soil | pH | Organic matter (g/kg) | Free iron oxides (g/kg) | Particle–size distribution (%) | | | | Soil texture (IUSS) |
				Clay ($< 2\,\mu$m)	Silt (2–20 μm)	Fine sand (20–200 μm)	Coarse sand (200–2,000 μm)	
Alluvial soil	7.7	17.2	43.3	17.2	27.5	54.5	0.8	clay loam
Grey degraded soil	5.7	13.8	4.3	6.7	15.7	74.1	3.5	sandy loam

Table 2. Approximate relative mineral contents (%) in the $< 2\,\mu$m clay fraction of the alluvial soil and grey degraded soil

Soil	Mc	Ch	Vt	St	Mx	Ch–Vt	Kt	Gt	Gb	Qr	Fd
Alluvial soil	40	8	12	2			24	2	tr.	9	3
Grey degraded soil	14	3			6	12	36	tr.	tr.	27	2

Abbreviations: Mc, mica; Ch, chlorite; Vt, vermiculite; St, smectite; Mx, mica/vermiculite/smectite mica/smectite mixed–layer mineral; Ch–Vt, chlorite–vermiculite intergrade; Kt, kaolinite; Gt, goethite; Gb, gibbsite; Qr, quartz; Fd, feldspars.

than did the alluvial soil, and contained some amounts of the mica/vermiculite/smectite mica/smectite mixed–layer mineral (6%). Vermiculite was not detected in the grey degraded soil. Instead, chlorite–vermiculite intergrade was present with the content (12%) corresponding to that of vermiculite in the alluvial soil. This suggested that chlorite–vermiculite intergrade would be a chloritization product of vermiculite. As for the minerals other than layer silicate minerals, the contents of goethite, gibbsite and feldspars in the grey degraded soil were comparable with those in the alluvial soil, whereas the quartz content (27%) was higher by three times for the former than for the latter. The lower mica and higher kaolinite and quartz contents in the grey degraded

Table 3. The initial (C_i, mg/L) and equilibrium (C_f, mg/L) concentrations of the metal nitrate solution, and the amount of metal adsorbed per unit mass of soil ($q_a 10^{-1}$, mg/kg) in the batch adsorption test

| Soil	C_i	Cu		Pb		Zn		Cd		
		C_f	$q_a 10^{-1}$	C_f	$q_a 10^{-1}$	C_f	$q_a 10^{-1}$	C_i	C_f	$q_a 10^{-1}$
Alluvial soil	50	0.3	49.7	0.0	50.0	0.4	49.6	5	0.0	5.0
	100	0.7	99.3	0.0	100.0	5.5	94.5	10	0.0	10.0
	250	10.5	239.5	0.0	250.0	82.5	167.5	20	0.1	19.9
	500	166.5	333.5	0.5	499.5	223.7	276.3	50	0.8	49.2
	1000	584.9	415.1	25.0	975.0	658.7	341.3	70	1.7	68.3
	1500	1066.5	433.5	209.9	1290.1	1121.6	378.4	100	3.9	96.1
	2000	1552.6	447.4	540.3	1459.7	1609.9	390.1			
Grey degraded soil	50	11.7	38.3	1.3	48.7	16.9	33.1	5	0.2	4.8
	100	48.4	51.6	1.4	98.6	51.6	48.4	10	0.5	9.5
	250	196.0	54.0	33.0	217.0	186.8	63.2	20	1.5	18.5
	500	444.3	55.7	243.1	256.9	427.1	72.9	50	9.4	40.6
	1000	943.3	56.7	734.4	265.6	905.6	94.4	70	18.2	51.8
	1500	1438.5	61.5	1220.5	279.5	1400.4	99.6	100	35.1	64.9
	2000	1932.9	67.1	1760.8	239.2	1894.7	105.3			
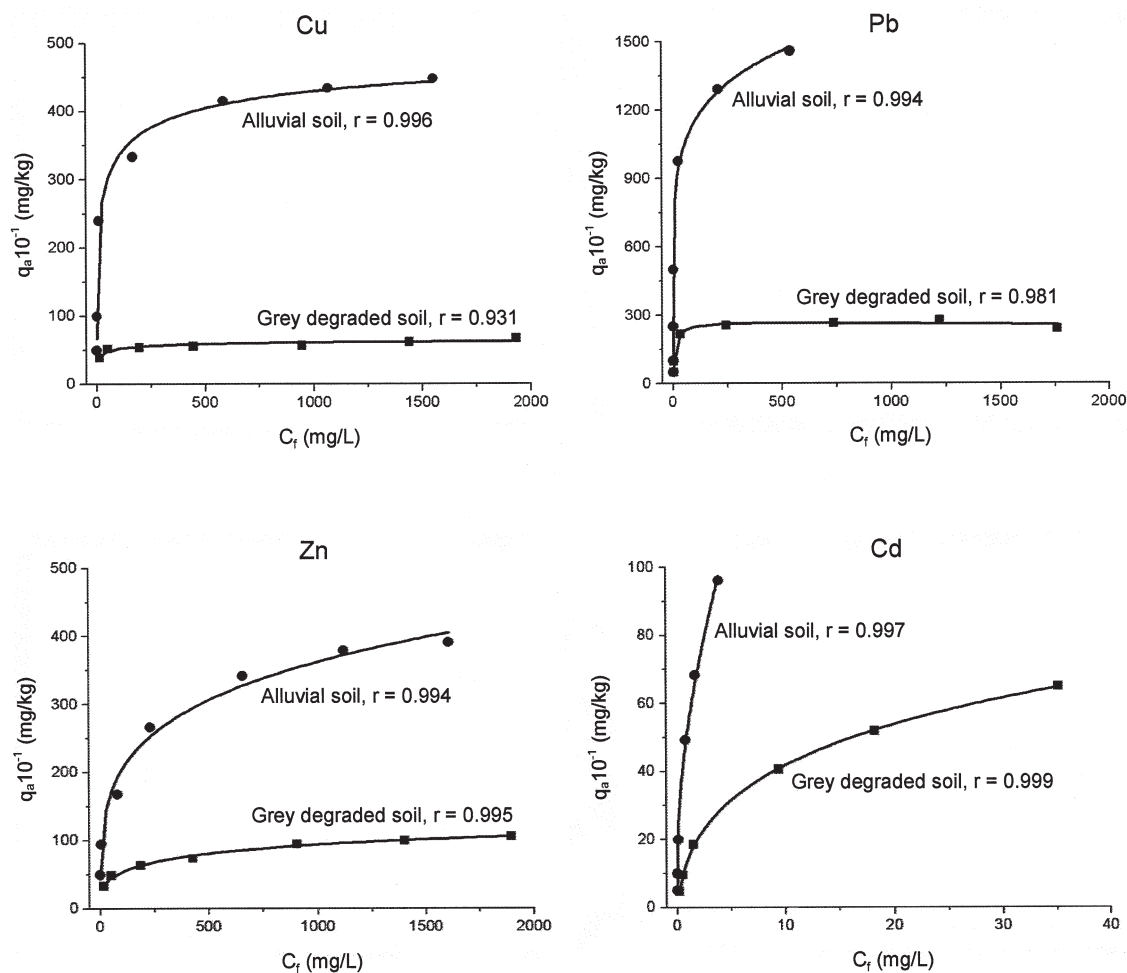
Fig. 2. Comparison of adsorption isotherms of Cu, Pb, Zn and Cd between the alluvial soil and grey degraded soil. The amount of heavy metals adsorbed ($q_a 10^{-1}$) is plotted against the equilibrium concentration (C_f) by using the Freudlich model.

soil have been reported by Do *et al.* (2002), who attributed it to decomposition of layer silicate minerals due to ferrolysis.

Adsorption capacity of heavy metals

Parameters from the batch adsorption test including the initial (C_i,) and equilibrium (C_f) concentrations of the metal nitrate solution, and the amount of metal adsorbed per unit mass of soil ($q_a 10^{-1}$) are given in Table 3. Adsorption isotherms of the respective heavy metals (Cu, Pb, Zn, and Cd) are plotted using OriginPro 7.5 software for the alluvial soil and grey degraded soil in Fig. 2. The relationship between $q_a 10^{-1}$ and C_f was well fitted to the Freudlich model with a very high correlation coefficient. In all cases, the adsorbed amount of any heavy metal at the same initial concentration was distinctly higher for the alluvial soil than for the grey degraded soil, suggesting the large adsorption capacity of heavy metals of the former in comparison with the latter. Variation in the adsorbed amount of heavy metals between the two soils was small at the low initial concentration levels but became larger at the higher initial concentration levels. This variation was dependent on the heavy metals, and was largest for Pb, followed by Cu and Zn, and smallest for Cd.

Figure 3 shows adsorption isotherms of Cu, Pb and Zn for the alluvial soil and grey degraded soil. The adsorption isotherm of Cd was not included here, because initial concentrations used in the batch adsorption test for Cd were different from those used for Cu, Pb and Zn. As shown in Fig. 3, the adsorption capacity within a soil was varied with heavy metals. In case of the alluvial soil, the adsorption rate or the ratio of $q_a 10^{-1}$ to C_i (data not shown) was kept at a high value while the equilibrium concentration remained in a very low level at initial concentrations between 50 and 100 mg/L for Zn, between 50 and 250 mg/L for Cu, and between 50 and to 1,000 mg/L for Pb. It meant that almost all amounts of added heavy metal were adsorbed by soil, and the adsorption capacity of heavy metals decreased in the sequence of Pb Cu Zn. At initial concentra-

tions over the above ranges, the adsorption rate was quickly reduced and hence the adsorbed amount of heavy metals became gradually constant. In the grey degraded soil, however, the adsorption rate was quickly reduced as exceeding initial concentrations of 50 mg/L for Cu and Zn and of 250 mg/L for Pb. The reduction in the adsorption rate was greater for Cu than for Zn, leading to the higher adsorbed amount for the latter than for the former at the initial concentration of 2,000 mg/L. Therefore, the adsorption capacity of heavy metals in the grey degraded soil followed the order of Pb Zn Cu.

In case of Cd, because the initial concentration range used in the batch adsorption test was different from that for Cu, Pb and Zn, direct comparison was difficult on the adsorption capacity with them. However, based on the comparison on the adsorbed amount with Cu, Pb and Zn at initial concentrations ranging from 50 to 100 mg/L, the adsorption capacity of Cd was estimated to be equivalent to that of Zn for the alluvial soil, and smaller than that of Pb but larger than those of Zn and Cu for the grey degraded soil.

Adsorption capacity of heavy metals in relation to heavy metal attributes and composition of adsorbing soil components

Among soil components, organic matter, free iron oxides, and clay minerals are considered important adsorbents for heavy metals (Bradl, 2004). The content of active 2:1–type silicate minerals in the clay faction was higher for the alluvial soil (62% as a total of mica, chlorite, vermiculite and smectite) than for the grey degraded soil (35% as a total of mica, chlorite, the mica/vermiculite/smectite mica/smectite mixed–layer mineral and chlorite–vermiculite intergrade). The organic matter, free iron oxides and clay contents were also higher for the alluvial soil than for the grey degraded soil. As a result, the adsorption capacity of heavy metals (Cu, Pb, Zn and Cd) of the former was distinctly larger than that of the latter, as mentioned in the above. In addition, the lower pH of the grey degraded
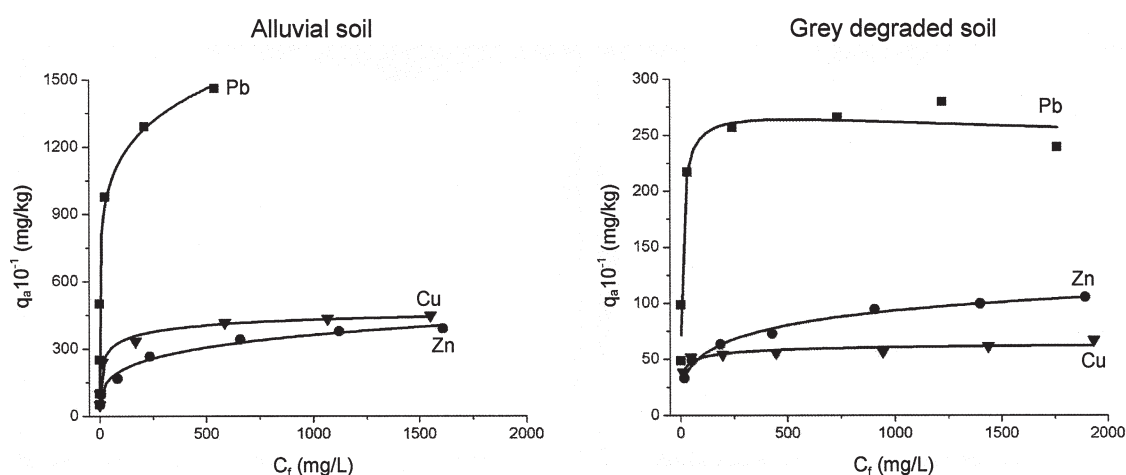

Fig. 3. Adsorption isotherms of Cu, Pb and Zn in the alluvial soil and grey degraded soil. The amount of heavy metals adsorbed ($q_a 10^{-1}$) is plotted against the equilibrium concentration (C_f) by using the Freudlich model.

soil would increase mobility of heavy metal ions.

Within a soil, the adsorption capacity of heavy metals followed the order of Pb   Cu   Zn for the alluvial soil and of Pb   Zn   Cu for the grey degraded soil. This would be related to the attributes of heavy metals and composition of adsorbing soil components. It has been recognized that the adsorption maxima of heavy metals by soil components such as organic matter, free iron oxides and clay minerals were often higher for Pb than for Cu and Zn (Helios *et al.*, 1995; Veeresh *et al.*, 2003). This might be a reason for the largest adsorption capacity of Pb observed in the soils of the present study.

In case of Cu, the adsorption maxima among soil components decreased in the order of organic matter   free iron oxides   clay minerals (Bradl, 2004), whereas in case of Zn, free iron oxides did not much contribute to its adsorption. Therefore, the adsorption capacity of Cu over Zn observed in the alluvial soil could be considered to be due to the high free iron oxides content of the soil. The order in the adsorption capacity of heavy metals observed in the alluvial soil of the present study has been found in many types of soil (Welp and Brümmer, 1999; Veeresh *et al.*, 2003).

For the grey degraded soil, the low organic matter and very low free iron oxides contents probably restricted the adsorption capacity of Cu. Active 2:1–type silicate minerals in the clay faction of the grey degraded soil were present with considerable amounts but they adsorbed Cu less strongly than organic matter and free iron oxides did. However, active 2:1–type silicate minerals exhibited a large fixing capacity for Zn (Bradl, 2004). For this reason, the adsorption capacity of Zn observed in the grey degraded soil was greater than that of Cu.

CONCLUSIONS

Two surface soil samples collected in Hanoi, Vietnam well represented alluvial soils and grey degraded soils in the area, since their chemical, physical and clay mineralogical properties were in accordance with those reported by previous studies for the same soil types. The alluvial soil had the high organic matter, free iron oxides, clay and active 2:1–type silicate minerals contents, and high pH value in comparison with those of the grey degraded soil. As a consequence, the adsorption capacity of heavy metals (Cu, Pb, Zn and Cd) was distinctly larger for the alluvial soil than for the grey degraded soil. Within a soil the adsorption capacity was related to the attributes of heavy metals and composition of adsorbing soil components. It decreased in the sequence of Pb   Cu   Zn for the alluvial soil and of Pb   Zn   Cu for the grey degraded soil.

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