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Contribution of Soil Components to Adsorption of Heavy Metals in Alluvial Soils and Grey Degraded Soils from Hanoi, Vietnam

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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 examination of adsorption of three heavy metals (Cu, Pb and Zn) by three adsorbing components (organic matter, free iron oxides and clay minerals). The results showed that Pb was adsorbed by all three components with the largest adsorbed amount and that Zn was adsorbed selectively by organic matter and clay minerals while Cu was selectively by organic matter and free iron oxides. The amount of heavy metals adsorbed per unit mass of adsorbing components was reduced in the sequence of organic matter＞clay minerals＞free iron oxides for Pb and Zn and of organic matter＞free iron oxides＞clay minerals for Cu. The difference in the adsorption capacity of heavy metals per unit mass of each component between the alluvial soil and grey degraded soil was attributed to the difference in the type of organic matter, form of free iron oxides or composition of clay minerals between them.

INTRODUCTION

In Hanoi City of Vietnam, grey degraded soils and alluvial soils are the main soil types and normally found in an associated distribution (Fig. 1). However, these soils have distinctly different properties from each other. In comparison with fertile alluvial soils, fertility of grey degraded soils has been declined 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). In consistency with this, we found that adsorption capacity of heavy metals in grey degraded soils was noticeably lower than that in alluvial soils (Bui *et al*., 2007).

It has been recognized that heavy metals are bound to various soil components, of which the most important ones are organic matter, free iron oxides, and clay minerals. However, it is hardly known how much a component contributes to adsorption of heavy metals in soil. The purpose of the present study is to examine adsorption of heavy metals by different adsorbing soil components of alluvial soils and grey degraded soils in Hanoi, Vietnam.

MATERIALS AND METHODS

Soils and their properties

In the present study, the same soil samples as the previous study (Bui *et al*., 2007) were used. 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 (Fig. 1). The properties of the alluvial soil were as follows: pH (H_2O), 7.7; organic matter, 17.2 g/kg; free iron oxides, 43.3 g/kg; clay (＜ 2 μm particle) in the whole inorganic fraction, 17.2%; and 2:1–type silicate minerals (as a total of mica, chlorite, vermiculite and smectite) in the clay fraction, 62%. Corresponding values for the grey degraded soil were 5.7, 13.8 g/kg, 4.3 g/kg, 6.7% and 35% (as a total of mica, chlorite, the mica/vermiculite/smectite～mica/smectite mixed–layer mineral and chlorite–vermiculite intergrade) and all were lower than the values for the alluvial soil. The adsorption capacity of heavy metals (Cu, Pb and Zn) was distinctly greater for the alluvial soil than for the grey degraded soil, and decreased in the sequence of Pb＞＞Cu＞Zn for the former and of Pb＞＞Zn＞Cu for the latter.

Pre–treatments and batch adsorption test

Triplicate sets of a sample containing 2.0 g air–dry soil each were exactly weighed into 500–mL tall beakers and marked as set–1, set–2 and set–3. Of the triplicate sets, set–2 and set–3 were added with 50 mL of 7% H_2O_2 while set–1 was with 50 mL of water. All sets were then placed on a hot plate and heated at 90 °C for about 2 h to decompose organic matter in set–2 and set–3. After cooling, the content of the beaker was transferred to a 50–mL centrifuge tube, followed by centrifugation and decantation, and washed with water 2 times. Two (2.0) g of sodium hydrosulfite and 25 mL of the citrate solution were added to the tube of set–3, while 25 mL water was added to the tubes of set–1 and set–2, followed by shaking reciprocally at room temperature for extraction of free iron oxides in set–3. After shaking, all sets were washed with water 2 times by centrifugation and decantation. These pre–treatments were done in triplicate for each soil sample, followed by the batch adsorp-

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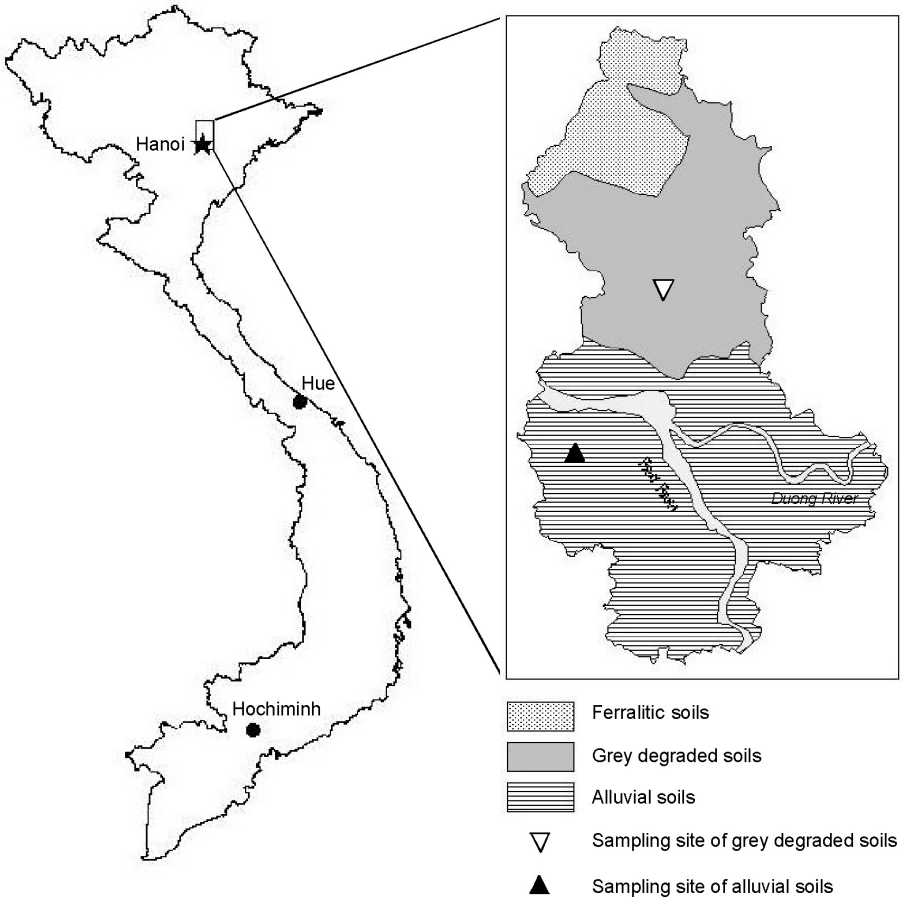

Fig. 1. Locations of sampling sites on the soil map of Vietnam.

tion test with three heavy metals of Cu, Pb and Zn.

Heavy metal solutions of Cu, Pb and Zn were prepared from the respective metal nitrate salts. Concentration of the solutions was fixed at 1500 mg/L, because adsorption of the heavy metals by the soils reached a maximum and became constant at that concentration (Bui *et al*., 2007). Three triplicate–sets were mixed with 20 mL of each of the 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 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.

Estimation of the amount of heavy metal adsorbed on soil components

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 amount of heavy metal adsorbed in set–1, set–2 and set–3 was assigned to q_a–1, q_a–2 and q_a–3, respectively, in which q_a–1 was equivalent to the amount of heavy metal adsorbed on all components, and the amount adsorbed on organic matter was estimated by subtracting q_a–2 from q_a–1 and that on free iron oxides by subtracting q_a–3 from q_a–2. Because both organic matter and free iron oxides were removed in set–3, q_a–3 would be the amount of heavy metal adsorbed mostly by 2:1–type silicate minerals.

RESULTS AND DISCUSSION

Effects of pre–treatments on the adsorption of heavy metals

In the procedure of the pre–treatments, washing of samples with water in several times would release and wash out heavy metals and some other cations in soil, leading to increase of sink for heavy metal adsorption. In addition, the soil pH would be increased by sample washing, especially for the grey degraded soil which naturally had the low pH value. This would prevent mobility of metal ions such as Cu and Zn and increase their adsorbed amount. As a result, the total amounts of

Table 1. The amount (mg/kg) of heavy metals adsorbed on three different components and in total

Soil	Heavy metal	Organic matter	Free iron oxides	Clay minerals	Total	Total without pre–treatments [1)]
Alluvial soil	Cu	666	1258	2718	4642	4335
	Pb	3443	1343	8485	13271	12901
	Zn	1000	61	3014	4075	3784
Grey degraded soil	Cu	185	57	908	1150	615
	Pb	1256	72	1772	3100	2795
	Zn	245	11	1494	1750	996

[1)] Quoted from the previous study (Bui *et al.*, 2007) at the initial concentration of 1500 mg/L after multiplying $q_a 10^{-1}$ by 10 to get the q_a value.

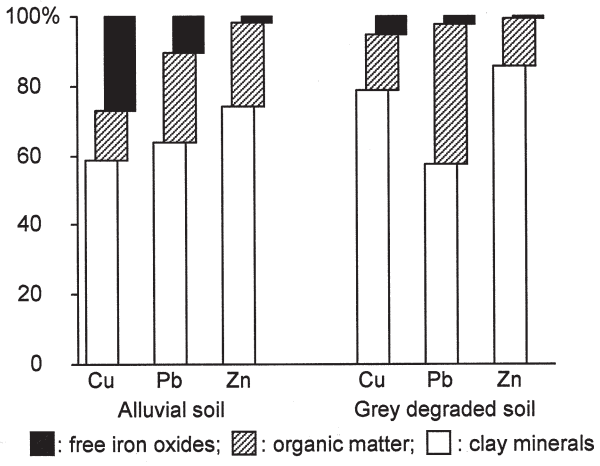

Fig. 2. The percentage of a heavy metal adsorbed on each component to the total adsorbed amount.

Cu, Pb and Zn adsorbed on pre–treated soils at the initial concentration of 1500 mg/L in the present study were larger than the corresponding values for non–pre–treated soils in the previous study (Bui *et al.*, 2007), and the total amounts of Cu and Zn adsorbed on the grey degraded soil were as high as twice in comparison with the amounts without pre–treatments (Table 1). However, the adsorption capacity of heavy metals was higher for the alluvial soil than for the grey degraded soil and decreased in the sequence of Pb>>Cu>Zn for the former and of Pb>>Zn>Cu for the latter, which was in accordance with results of the previous study (Bui *et al.*, 2007).

Adsorption of heavy metals by soil components

The amounts of heavy metals adsorbed on three different components are given in Table 1 and the percentages of a heavy metal adsorbed on each component to the total adsorbed amount are shown in Fig. 2. It should be noted that after removal of organic matter and free iron oxides, silicate minerals and oxide/hydroxide minerals other than iron remained in soil. Under such situation, adsorption of heavy metals was not totally but mostly due to clay minerals, and hence the term of clay minerals was used as a representative of adsorbing soil components after the pre–treatments for removal of organic matter and free iron oxides.

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 was the case for the alluvial soil and grey degraded soil from Hanoi in the present study. Between Cu and Zn, the latter was adsorbed with somewhat large amounts by organic matter and clay minerals while with much small amounts by free iron oxides in comparison with the former. Therefore, in the alluvial soil having the high free iron oxides content, the total amount adsorbed by all three components was larger for Cu than for Zn. This situation was reversed in the grey degraded soil which had the low free iron oxides content.

Because clay minerals were in the largest content among three adsorbing components, they contributed to occupation of 57.2 to 85.4%, depending on the type of heavy metal and soil, of the total amount of heavy metals adsorbed. Adsorption by organic matter attained to 14.0 to 40.5% of the total amount of heavy metals adsorbed, whereas contribution of free iron oxides to the total amount of heavy metals adsorbed was normally less than 10%, except adsorption of Cu in the alluvial soil (27.1%).

Adsorption of heavy metals based on the unit mass of soil components

The amounts of heavy metals adsorbed per unit mass of three components were estimated and are given in Table 2. For organic matter and free iron oxides, estimation was simply done by dividing the amount adsorbed on the respective components (Table 1) by their contents written in **Materials and Methods**. For clay minerals, the clay mineral content in soil (unit: %) was first calculated from the 2:1–type silicate minerals content in the clay fraction and the clay content in soil. The unit was then converted into g/kg to enable such estimation.

As shown in Table 2, the amounts of Cu, Pb and Zn adsorbed per unit mass of organic matter and of Cu and Pb per unit mass of free iron oxides were larger for the alluvial soil than for the grey degraded soil. In contrast, the amounts of heavy metals adsorbed per unit mass of clay minerals were larger for the grey degraded soil than for the alluvial soil. This would be attributed to the differences in type of organic matter, form of free iron oxides or composition of clay minerals between the two soil types. Concerning the kind of adsorbents, the

Table 2. The amount (mg/g) of heavy metals adsorbed per unit mass of three components

Soil	Heavy metal	Organic matter	Free iron oxides	Clay minerals
Alluvial soil	Cu	39	29	6
	Pb	200	31	32
	Zn	58	1	9
Grey degraded soil	Cu	13	13	8
	Pb	91	17	53
	Zn	18	3	10

adsorbed amount of individual heavy metal decreased in the sequence of organic matter>clay minerals>free iron oxides for Pb and Zn and of organic matter>free iron oxides>clay minerals for Cu.

CONCLUSIONS

Adsorption of heavy metals by different soil components was examined for the alluvial soil and grey degraded soil from Hanoi, Vietnam. The amount of heavy metals adsorbed decreased in the order of Pb>>Zn>Cu for organic matter and clay minerals and of Pb>Cu>>Zn for free iron oxides. In other context, the amount of heavy metals adsorbed per unit mass of soil components decreased in the sequence of organic matter>clay minerals>free iron oxides for Pb and Zn and organic matter>free iron oxides>clay minerals for Cu. The difference in the adsorption capacity of individual heavy metal per unit mass of each component observed between the alluvial soil and grey degraded soil was attributed to the difference in the type of organic matter, form of free iron oxides or composition of clay minerals between them.

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