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Lead and Zinc Adsorption by Agricultural Soils from Trade Villages in Bac Ninh Province, Northern Viet Nam

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The objective of the current paper is to assess the heavy metal status and adsorption behavior of heavy metals in agricultural soils from Vanmon Commune, Yenphong District and Chaukhe Commune, Tuson District of Bacninh Province, located in the Red River Delta region, northern Vietnam. Total and available concentrations of Cd, Cu, Pb and Zn were determined for the soils collected in Vanmon and Chaukhe Communes which are engaged in recycling of steel as a trade village. Total concentrations of twenty-one soils ranged between 0.18 and 0.62 mg/kg for Cd, 17.9 and 39.6 mg/kg for Cu, 19.5 and 45.2 mg/kg for Pb, and 25.6 and 236.8 mg/kg for Zn. Based on the comparison with the Vietnamese standard for heavy metal concentrations in agricultural soils, total concentrations of those heavy metals were regarded to be in a normal range, except Zn at two sites in a village of Chaukhe Commune, Tuson District. In the correlation between total and available concentrations of heavy metals, the total Pb concentration showed a significant correlation with the total concentrations of Zn and Cd (1% level), and Cu (5% level). The concentration of available Zn extracted by 0.1 M HNO₃ was found to be higher for the examined soils than for the other agricultural soils in the Red River Delta. The adsorption of Pb and Zn by the agricultural soils, carried out in the concentrations ranging from 100 to 7,500 mg/L for Pb and from 1 to 2,500 mg/L for Zn, indicated that adsorption isotherms of both heavy metals were well fitted to the Freundlich equation. The adsorption capacity of the agricultural soils was larger for Pb than for Zn.

INTRODUCTION

In Vietnam, rapid industrialization and motorization due to shift of planned economy to market-oriented economy have caused severe environmental pollution in big cities and neighboring areas (Ho *et al.*, 1998; Ho and Egashira, 2000; Egashira and Kurosawa, 2005). In addition, Vietnam has a long history of recycling of steel in a commune or village level in the Red River Delta. Those communes or villages are called a trade village. Recent scaling-up in recycling of steel by national and local economic development has a possibility of heavy metal pollution of soils in and around a trade village (Ho and Nguyen, 2003; Nguyen *et al.*, 2005).

In Vietnam, most of studies on the heavy metal pollution of soils remain in the evaluation of pollution status by measuring the concentration of heavy metals. Study on the adsorption of heavy metals by soils is limited until now. In the present study, agricultural soils were collected around trade villages of Chaukhe Commune, Tuson District and Vanmon Commune, Yenphong District of Bacninh Province, and the pollution status was evaluated by measuring total and available concentrations of Cd, Cu, Pb and Zn, followed by characterization of Pb and Zn adsorption by the soils.

MATERIALS AND METHODS

Location of soil sampling

Twenty-one soil samples were taken from agricultural soils in Chaukhe Commune of Tuson District and Vanmon Commune of Yenphong District, Bacninh Province, located in the Red River Delta region and neighboring to Hanoi City, northern Vietnam. These communes, known as a trade village, have been engaged in recycling of steel for long time. It is speculated that various heavy metals are accumulated in different levels in soils in and around villages/communes.

Among 21 samples, 8 samples of D-1 to D-8 were collected from Chaukhe Commune, Tuson District, and 13 samples of V-11 to V-23 were from Vanmon Commune, Yenphong District. The soils in Chaukhe Commune, Tuson District are classified as alluvial soils by the Vietnamese soil classification system and the soils in Vanmon Commune, Yenphong District are as grey degraded soils. Sampling sites were positioned within 50 to 100 m from the trade villages and on the medium-level and low places in the relatively high land of the communes. The soils were air-dried at room temperature, disaggregated using a porcelain pestle and mortar, passed through a 2-mm sieve, and stored in sealed polyethylene bags until use for chemical analysis and adsorption experiment.

Determination of pH and organic carbon

The pH was measured in the suspension having a soil:solution ratio of 1:5, and organic carbon (C) 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.

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Determination of concentrations of total and available heavy metals

One g of air-dry soil was digested with the HNO_3 acid treatment to determine the concentration of total heavy metals. In the determination of the concentration of available heavy metals ten g of air-dry soil was extracted with 0.1 M HNO_3 with a soil:solution ratio of 1:10 (Ho and Egashira, 2001). Cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) were targeted in the present study for their priority in the soil pollution control in the Red River Delta region. Their concentrations were measured by an atomic absorption spectrophotometer (AAS).

Adsorption experiment of Pb and Zn by agricultural soils

The adsorption experiment of Pb and Zn by agricultural soils was carried out with nine and eight different concentrations, respectively, ranging from 100 to 7,500 mg/L for Pb and from 1 to 2,500 mg/L for Zn. Samples D-1 and D-3 through D-6 in Chaukhe Commune and samples V-11, V-14 and V-23 in Vanmon Commune were selected for the adsorption experiment.

The batch equilibrium test was used for the adsorption experiment. A soil:solution ratio of 1:10 was employed as recommended by Li (2002). Air-dry soil equivalent to approximately 2.5 g in dry-weight was mixed with 25 mL of the heavy metal solution in a 50-mL polypropylene centrifuge tube. The centrifuge tube was shaken for 24 hours followed by centrifugation at room temperature at about 2,500 rpm for 15 minutes. Lead and Zn concentrations of the solution before and after the 24-h shaking at room temperature were measured by AAS to determine the adsorbed amount of heavy metals by soil. The experiment was done in duplicate to ensure the accuracy of determination and the relative deviation of the duplicate values was usually less than 5%.

Lead nitrate and zinc nitrate solutions of various concentrations kept at pH 4.0 were used in the adsorption experiment to prevent the adsorption process from contamination of precipitated forms of Pb and Zn. Concentrations of the solutions were 100, 250, 500, 1000, 1500, 2000, 2500, 5000, 7500 mg/L for Pb and 1, 10, 100, 500, 1000, 1500, 2000, 2500 mg/L for Zn.

ADSORPTION ISOTHERM

The heavy metal concentration adsorbed on the adsorbent is calculated with the following equation:

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

where q_a is the Pb or Zn adsorption concentration (mg/kg); C_i is the initial concentration of the lead nitrate or zinc nitrate solution (mg/L); C_f is the equilibrium (final) Pb or Zn concentration in solution after 24-h shaking (mg/L); V is the volume of the lead nitrate or zinc nitrate solution (L) used in the batch adsorption test; and M is the soil mass (kg). In this study, M was

obtained by dividing the mass of air-dry soil by $(1 + w)$, where w is the moisture content of air-dry soil. In this way milligrams of Pb or Zn retained per kilogram of dry-soil could be obtained. q_a was plotted against the equilibrium concentration to prepare the adsorption isotherm for Pb and Zn.

The adsorption isotherm was modeled by applying the Freundlich equation. The Freundlich equation is written as

$$q_a = K_f C^n, \quad n < 1$$

where K_f and n are the empirical constants, and q_a is the adsorption concentration (mg/kg) of Pb or Zn and C is the equilibrium (final) Pb or Zn concentration (mg/L). The goodness of fit of the Freundlich equation to experimental data was checked by comparison of the correlation coefficient "r" and used in all calculations with the confidence level set at 95%.

RESULTS AND DISCUSSION

pH and organic matter content of agricultural soils

The pH and organic matter content of agricultural soils are shown in Table 1. The pH (H_2O) of the soils ranged between 4.29 and 6.21, suggesting the strongly to weakly acidic condition of them. The organic matter content of 21 soils was in a range between 15.2 and 46.2 g/kg and exceeded by 1.4 to 2.4 times, except sample V-23, the value of 19.4 g/kg which is an average of the organic matter content reported to agricultural soils of the Red River Delta between 1973 and 1982 (Nguyen *et al.*, 1997). This tendency can be explained by the increasing application of organic manure and residues by farmers after Vietnam Government executed the new land policy in 1993, by which farmers were permitted to use agricultural soils for 20 years in the cultivation of annual crops.

Concentrations of total and available heavy metals in agricultural soils

Concentrations of total heavy metals in agricultural soils are shown in Table 1, and ranged between 0.18 and 0.62 mg/kg for Cd, 17.9 and 39.6 mg/kg for Cu, 19.5 and

Table 1. The pH, organic matter content, and total and available heavy metal concentrations in agricultural soils of Bacninh Province

Commune	Soil sample	pH (H ₂ O)	Organic matter (g/kg)	Total heavy metal (mg/kg)				Available heavy metal (mg/kg)			
				Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd
Chaukhe	D-1	4.29	46.2	45.2	27.7	117.6	0.62	13.4	10.4	38.0	0.40
	D-2	5.53	46.0	40.1	28.0	134.8	0.49	10.4	11.0	36.7	0.36
	D-3	4.71	36.8	28.5	21.8	147.3	0.31	6.3	7.3	54.0	0.19
	D-4	5.09	39.5	36.7	30.8	232.9	0.23	10.1	11.2	71.3	0.16
	D-5	6.20	41.1	34.1	34.5	236.8	0.27	6.5	11.5	67.8	0.13
	D-6	5.11	44.8	42.0	37.3	164.2	0.44	12.9	12.9	45.5	0.19
	D-7	5.41	32.9	29.6	23.9	129.8	0.27	8.6	9.3	34.3	0.15
	D-8	5.17	30.2	27.0	26.6	107.9	0.44	6.1	9.4	26.3	0.20
Vanmon	V-11	5.36	27.0	20.3	18.8	25.6	0.27	5.6	8.2	4.4	0.13
	V-12	5.45	32.2	22.5	28.6	40.9	0.27	6.6	14.2	15.1	0.24
	V-13	4.91	27.4	22.7	17.9	32.3	0.23	4.9	6.6	7.9	0.16
	V-14	5.39	31.3	40.0	34.6	114.0	0.27	12.2	14.4	35.3	0.21
	V-15	5.74	35.5	23.1	23.0	29.0	0.18	6.0	9.8	7.6	0.09
	V-16	6.21	36.8	19.5	19.7	34.5	0.18	4.9	8.9	12.4	0.14
	V-17	6.14	30.3	31.7	29.8	52.0	0.27	11.7	15.0	18.0	0.17
	V-18	5.52	33.2	20.7	21.1	32.8	0.18	5.7	9.8	9.8	0.15
	V-19	6.12	34.0	34.5	22.2	31.5	0.23	13.7	9.6	9.8	0.18
	V-20	5.85	33.6	25.6	30.9	35.6	0.27	8.2	14.4	10.5	0.15
	V-21	5.65	29.5	23.0	39.6	40.1	0.22	7.3	18.7	9.4	0.16
	V-22	5.34	35.9	28.4	33.3	39.7	0.18	8.9	15.8	11.3	0.14
	V-23	5.62	15.2	40.2	37.0	52.0	0.18	15.3	16.6	16.5	0.10

45.2 mg/kg for Pb, and 25.6 and 236.8 mg/kg for Zn. Based on the comparison with the Vietnamese standard for heavy metal concentrations in agricultural soils (Ministry of Science and Environment, Vietnam, 2002), total concentrations of those heavy metals were regarded to be in a normal range, except Zn at two sites in a village of Chaukhe Commune, Tuson District, where total concentrations of Zn were in the level of 230–240 mg/kg. The soils in the present study were collected from the low to medium-level places of agricultural land around trade villages engaged in recycling of steel for long time. But, no sign of soil pollution by heavy metals was indicated, except slight accumulation of Zn at two out of 21 sites.

Concentrations of available heavy metals extracted with 0.1 M HNO₃ are shown in Table 1. The availability of heavy metals can be assessed by the concentration of the available form. Concentrations of available heavy metals ranged from 0.09 to 0.40 mg/kg for Cd, from 6.6

to 18.7 mg/kg for Cu, from 4.9 to 15.3 mg/kg for Pb, and from 4.4 to 71.3 mg/kg for Zn. The concentration of available Zn was found to be higher for the present agricultural soils than for the other agricultural soils in the Red River-Delta (Ho and Egashira, 2001; Ho and Nguyen, 2003), suggesting that Zn is a more available or susceptible metal to plants in the examined area.

Correlation between total and available heavy metal concentrations, and with pH and organic matter content in agricultural soils

The correlation coefficients between total and available heavy metal concentrations, and with pH and organic matter content for agricultural soils are given in Table 2. In the total heavy metal concentration, Pb showed a significant correlation with Cd, Cu and Zn at 1% or 5% level, but no significant correlation was observed for any combination between Cu, Zn and Cd. Similarly, no significant correlation between total con-

Table 2. Correlation coefficients between total and available heavy metal concentrations, and with pH and organic matter content for agricultural soils of Bacninh Province

Item	Available heavy metal				Total heavy metal			
	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd
pH	-0.273	0.088	-0.254	-0.552**	-0.069	0.276	-0.284	-0.495*
OM	0.042	-0.233	0.545*	0.573**	0.361	0.022	0.546*	0.582**
Available Pb		-0.429	-0.201	0.327	0.862**	0.513	0.185	0.307
Available Cu			-0.122	-0.074	0.223	0.868**	-0.119	-0.154
Available Zn				0.267	0.587**	0.302	0.985**	0.385
Available Cd					0.523*	0.032	0.248	0.852**
Total Pb						0.516*	0.586**	0.571**
Total Cu							0.328	0.107
Total Zn								0.408

OM: organic matter content.

* and ** mean significance at 5% and 1% levels, respectively.

centrations of Cd, Cu, and Zn was reported by Ho and Egashira (1999) for agricultural soils in Tuliem and Thanhtri Districts of Hanoi City. Concerning the available heavy metal concentration, no significant correlation was observed for all combinations. The total and available concentrations showed a highly significant correlation in each of four heavy metals.

Cadmium showed a significant correlation with the organic matter content in both total and available concentrations at 1% level. Variation of the available and

total Cd concentrations of agricultural soils can be well explained by variation of the organic matter content, suggesting that artificial contamination or pollution by Cd is negligible or very low.

Mobility of heavy metals in agricultural soils

The available concentration of heavy metals had a strong and positive correlation with its total concentration (Table 2). The relative mobility of a heavy metal should be assessed based on the ratio of the available to

Fig. 1. Adsorption isotherms of Zn by agricultural soils.

total concentrations. If we follow this idea, the mobility of heavy metals in the present study decreased in the order of Cd (0.58) > Cu (0.36) > Zn (0.29) > Pb (0.26) for alluvial soils and of Cd (0.69) > Cu (0.45) > Pb (0.31), Zn (0.30) for grey degraded soils, since the ratio of the available to total concentrations decreased in this sequence as the average ratio is shown in the parenthesis. For the respective heavy metals, excluding Zn, its mobility was larger for grey degraded soils than for alluvial soils.

Adsorption of Pb and Zn by agricultural soils

The adsorption of Pb and Zn by agricultural soils was carried out by the batch adsorption experiment in

concentrations ranging from 100 to 7,500 mg/L for Pb and from 1 to 2,500 mg/L for Zn. The adsorption isotherms, a graphical relationship between the adsorbate concentration on the adsorbent and the equilibrium concentration of adsorbate in solution, for both Zn and Pb are presented in Figs. 1 and 2, respectively. This is commonly used to represent the adsorption capacity of an adsorbent, such as the Freundlich adsorption isotherm (Li, 2002). Adsorption isotherms of Zn and Pb by agricultural soils were satisfactorily described by the Freundlich equation with determination coefficient over 0.87 (Figs. 1 and 2). The adsorption concentration of both heavy metals increased first rapidly and then gradually with the increased equilibrium concentration.

Fig. 2. Adsorption isotherms of Pb by agricultural soils.

Table 3. Empirical constants in the Freundlich equation for Pb and Zn adsorption by agricultural soils

Commune	Soil sample	Pb		Zn	
		K_f	n	K_f	n
Chaukhe	D-1	3.52	0.539	1.81	0.620
	D-3	3.88	0.466	1.82	0.629
	D-4	4.81	0.342	2.31	0.558
	D-5	5.46	0.302	2.29	0.597
	D-6	4.74	0.356	2.07	0.614
Vanmon	V-11	3.85	0.409	2.33	0.562
	V-14	5.29	0.234	2.18	0.572
	V-23	4.39	0.348	2.18	0.586

It was considerably higher for Pb than for Zn at a specified equilibrium concentration irrespective of the soils.

Empirical constants of the Freundlich equation, K_f and n, are given in Table 3. As can be seen from Table 3, the values of " K_f " and "n" somewhat varied with soils but not essentially different between Chaukhe and Vanmon Communes, except the "n" value in the Pb adsorption which tended to be higher for soils from Chaukhe Commune than for soils from Vanmon Commune. The K_f value was always higher for Pb than for Zn and varied from 3.52 to 5.46 for Pb and from 1.81 to 2.33 for Zn. It means that adsorbability by the agricultural soils is larger for Pb than for Zn, similar to the result of Lin and Chen (1998). The present K_f values for the Pb adsorption by the agricultural soils were markedly low compared with those for the Pb adsorption by zeolite (Myroslav *et al.*, 2006).

The adsorption concentrations of Pb increased following the Freundlich curve when the Pb concentration in the equilibrium solution was increased (Fig. 2). All the agricultural soils behaved similarly with regard to the Pb adsorption at low Pb concentrations. At intermediate to high Pb equilibrium concentrations, however, the adsorption concentration of Pb varied between the soils of Chaukhe and Vanmon Communes. The Pb adsorption concentration was higher for alluvial soils in Chaukhe Commune than for grey degraded soils in Vanmon Commune at the fixed equilibrium concentration. It suggests that grey degraded soils have a higher risk of Pb pollution to the environment, in addition to their low soil fertility. Sample V-23 which was estimated to be in the stage of the most advanced soil degradation among the soils, based on the lowest organic matter content, showed the highest concentration of available Pb (Table 1). In contrast to Pb, the adsorption concentration of Zn was not substantially different between alluvial soils in Chaukhe Commune and grey degraded soils in Vanmon Commune in the whole equilibrium concentration examined.

In other context, as more Pb^{2+} ions were adsorbed onto the soil surface, they replaced more H^+ ions, leading to lowering the pH. This phenomenon has been found by Li and Li (2000). Lowering pH has two effects: increasing the concentration of competing cations and decreasing the surface negative charge as less dissociation of H^+ ions occurs from functional groups

(Sparks, 1995). Both effects likely cause an underestimation of the adsorption capacity of soils at the higher equilibrium concentration of heavy metals.

CONCLUSIONS

The adsorption isotherms of Pb and Zn by the agricultural soils sampled around trade villages, obtained from the batch adsorption experiment, were well fitted to the Freundlich equation, which was good for modeling of the heavy metal adsorption by agricultural soils at low initial solution concentrations. The adsorption capacity of the agricultural soils was larger for Pb than for Zn.

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