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Heavy Metal Status of Agricultural Soils in Tuliem and Thanhtri Districts of Hanoi City, Vietnam

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Based on the comparison with several reference values including the Vietnam standard for heavy metal contents in soils and the correlation with selected soil properties, total heavy metals were regarded to be in a normal range for soils, except for Cu in one soil which was collected from the vegetable field and supposed to be suffered from heavy application of pesticide. Pollution of agricultural soils by heavy metals is still to be limited and very low in Tuliem and Thanhtri districts of Hanoi city. In contrast, one river–sediment sample collected from the Kimngun River flowing through the area contained various heavy metals by 3.5 to 12 times higher than the averages of agricultural soils, except for Mn, suggesting severe accumulation of different heavy metals in the river bed probably due to industrial discharge.

INTRODUCTION

Hanoi is the capital of Vietnam and located in the deltaic plain of the Red River in Northern Vietnam. Climate of the Red River delta is dominated by subtropical monsoon with mean annual rainfall of 1,600–1,900 mm. The total area of Hanoi city is about 1,000 km^2 and comprises 7 prefectures (Haibatrung, Badinh, Hoankiem, Dongda, Tayho, Caugiay, and Thanhxuan) in the center and 5 districts (Tuliem, Thanhtri, Donganh, Gialam, and Socson) around (Fig. 1). Population of Hanoi city is 2.25 million (Hanoi Statistical Office, 1996) and is increasing at the annual rate of more than 2%. Since renovation (doi moi) in 1986, Hanoi has experienced rapid economical development and explosions without city planning, which have produced a lot of environmental problems for human life and agricultural production.

Tuliem and Thanhtri districts are situated in the western to southern part of Hanoi city (Fig. 1). The total area of the districts is 20,282 ha. About 40% is the agricultural land which has been one of the most productive area. Main agricultural products are rice and vegetables. They are supplied to the markets of Hanoi city throughout the year. After doi moi, intensification and diversification of cropping system were advanced, leading to the great increase of farmers' income. However, urbanization and industrialization were pushed in the districts. Twenty–two manufacturing industries are now in operation which consume nearly 35,000 tons of coal and 2,000 tons of petrol per year (Ho *et al.*, 1998a). In addition, rapid population growth was brought about. Now Tuliem and Thanhtri districts have the population of nearly one million and are the densely–populated area in Hanoi city. Rapid urbanization and industrialization, along with motorization, have seriously impacted agricultural production: diversified use and loss of agricultural lands, pollution of water and soils, and decline in the soil fertility. Among these problems, water and soil pollution is the most urgent thing to be controlled, and monitoring of agricultural water and soils started in 1995 in Hanoi city sponsored by

Hanoi Scientific and Environmental Office (Ho *et al.*, 1998a). Possible sources of water and soil pollution are industrial discharge, municipal wastes, vehicle emissions, and agricultural chemicals.

In the present study, the focus was placed on the heavy metal pollution of agricultural soils of Tuliem and Thanhtri districts of Hanoi city. Samples were collected in ten locations of the districts and their heavy metal pollution was evaluated by comparing the total heavy metal contents with reference values for soils and by examining the correlation between total heavy metal contents and selected soil properties.

MATERIALS AND METHODS

1. Location and soil samples

Sampling sites of soils (No. 1 to No. 9) and the river system in Tuliem and Thanhtri districts are shown in Fig. 1. One river–sediment sample was collected for comparison and the sampling site (No. 10) is also shown in Fig. 1. Brief description of these samples are given in Table 1. Nine soil samples were collected to cover the whole study area and one river–sediment sample was taken from the river bed of the Kimnguu River. Soil samples were taken from paddy and upland fields, depending on their relative distribution, and at different relative land heights in the region. All samples were taken out of the surface 15–cm layer in July, 1997. After collection, they were immediately air–dried, ground with a ceramic pestle, passed through a 1–mm sieve and preserved in

Table 1. Brief description of soil and river–sediment samples used in the study.

Sample No.	Location: District	Location: Commune	Land use (crop)	Relative land height in the region	Soil classification by FAO/UNESCO
1	Tuliem	Taytuu	Upland (vegetables)	High	Orthi–Umbri–Eutric Fluvisols
2		Phudien	Paddy (rice–rice)	Low	Endo–Orthi–Eutric Fluvisols
3		Xuanphuong	Paddy (rice–rice–vegetables)	Middle	Orthi–Plinthi–Eutric Fluvisols
4		Yenhoa	Paddy (rice–rice)	Lowest (marshy)	Epi–Stagni–Eutric Gleysols
5	Thanhtri	Mydinh	Paddy (rice–rice)	Low	Endo–Orthi–Eutric Fluvisols
6		Thanhliet	Paddy (rice–rice)	Middle	Orthi–Plinthi–Eutric Fluvisols
7		Tuhiep	Paddy (spinach)	Low	Endo–Orthi–Eutric Fluvisols
8		Lienninh	Paddy (rice–rice–vegetables)	Middle	Orthi–Plinthi–Eutric Fluvisols
9		Daiang	Paddy (rice–rice)	Lowest (marshy)	Epi–Stagni–Eutric Gleysols
10		Tranphu	–	River bed	–

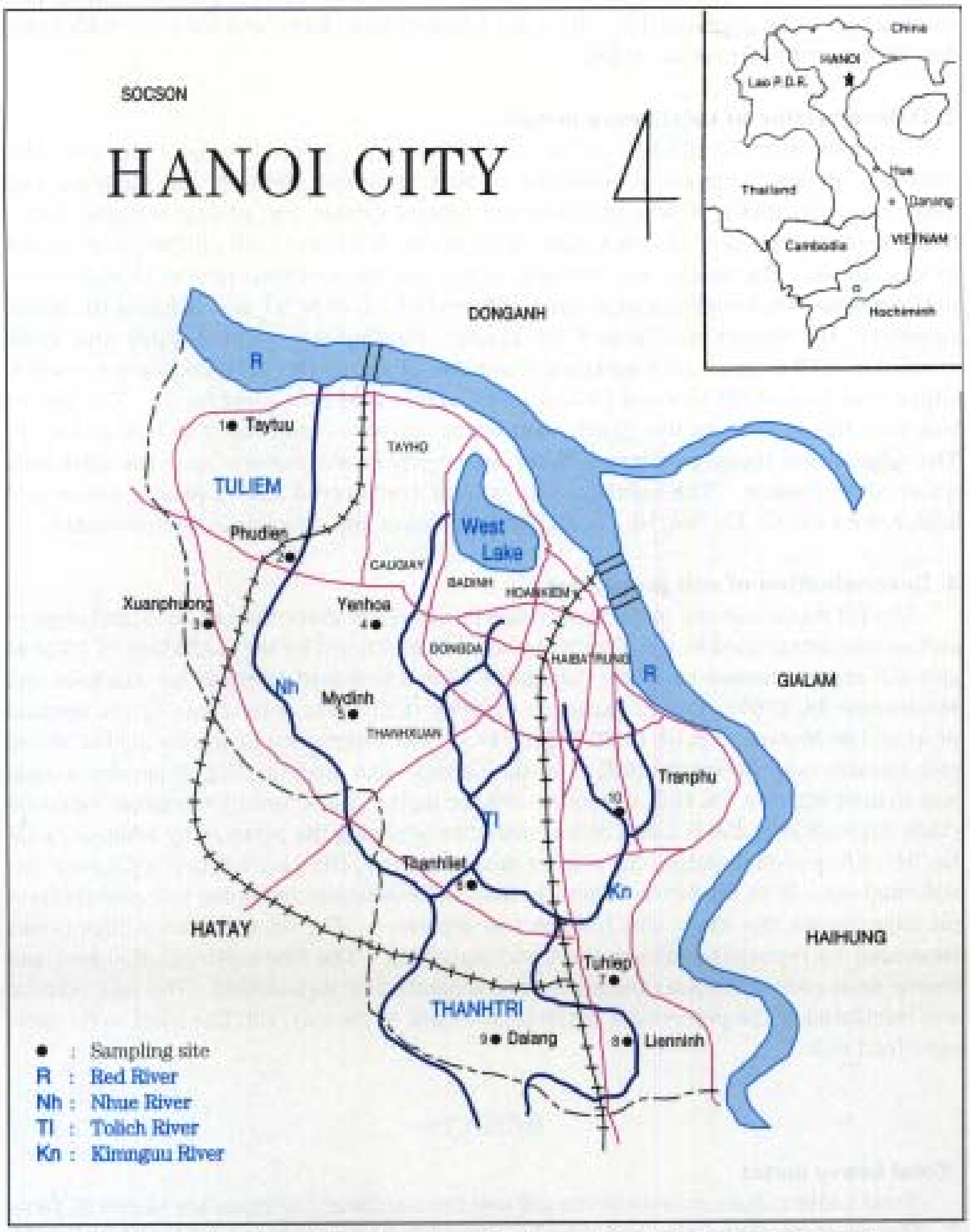

Fig. 1. Sampling sites and the river system in Tuliem and Thanhtri districts of Hanoi city.

plastic bottles. They were brought to Japan by air and subjected to chemical and physical analyses. Clay mineralogically, all the samples were found to be quite similar to one another and to be dominated by clay mica followed by chlorite and kaolinite with being devoid of smectite (Ho *et al.*, 1998b).

2. Determination of total heavy metals

Digestion with the HF–HNO_3–$HClO_4$ acid treatment was used to determine the total contents of heavy metals (Committee of Soil Standard Methods for Analyses and Measurements, 1986). One g of pulverized air–dry sample was exactly weighed into a teflon beaker and placed on a hot plate. Five mL of $HClO_4$ and 5 mL of HNO_3 were added to the sample. The beaker was covered, heated for 3 h, and then heated without cover until dryness. After cooling and gradual addition of 5 mL of $HClO_4$ and 10 mL of HF in this sequence, the beaker was heated for 15 min. Heating was once stopped and again continued until dryness after addition of another 10 mL of HF. The beaker was cooled, added with 5 mL of 6M HCl and 1 mL of HNO_3, and heated with cover for 1 h. The beaker was then filled–up to its two–thirds with water, covered, and heated to boiling for 2 h. The solution was transferred into a 50–mL volumetric flask and made up to the mark with water after cooling. The solution was quickly transferred into a plastic bottle and analyzed for Cd, Cr, Cu, Mn, Ni, Pb, and Zn by a atomic absorption spectrophotometer.

3. Determination of soil properties

The pH was measured in the suspension having a soil:water ratio of 1:2.5; and organic carbon was determined by the Tyurin method and multiplied by the coefficient of 1.724 to give the organic matter content (Committee of Soil Standard Methods for Analyses and Measurements, 1986). Cation exchange capacity (CEC) was determined by the method proposed by Muramoto *et al.* (1992). Free Fe_2O_3 was determined by the method of Mehra and Jackson (van Reeuwijk, 1992). In the particle–size analysis, 10 g of air–dry sample was treated with hot 7% H_2O_2 to remove organic matter, dispersed by ultrasonic vibration (tank–type; 38 kHz, 250 W), and deflocculated by adjusting the pH to 10 by addition of 1M NaOH. After sedimentation for a fixed period of time, the clay fraction ($<2\,\mu m$) was siphoned out. With repetition of sonification–sedimentation–siphoning with intermittent pH adjustments, the whole clay fraction was separated. The silt fraction (2–20 μm) was separated by repeated sedimentation and siphoning. The fine sand (20–200 μm) and coarse sand (200–1,000 μm) fractions were separated by wet–sieving. The clay content was calculated as the percentage to the total weight of the clay, silt, fine sand, and coarse sand fractions.

RESULTS

Total heavy metal

Total heavy metal contents of the soil and river–sediment samples are shown in Table 2. The contents of the nine soil samples ranged between 0.16 and 0.36 mg kg^{-1} for Cd, 62.5 and 112.8 mg kg^{-1} for Cr, 40.1 and 73.2 mg kg^{-1} for Cu, 378 and 750 mg kg^{-1} for Mn, 33.6 and 66.0 mg kg^{-1} for Ni, 31.9 and 45.3 mg kg^{-1} for Pb, and 98.2 and 137.2 mg kg^{-1} for Zn. The highest content of the heavy metals was observed for sample No. 6 which had the highest clay content among the soil samples (Table 6), except for Cd and Cu. The highest content of Cd was obtained for sample No. 7 taken from paddy field cultivated for spinach. In case of Cu, the highest content was obtained in sample No. 1 taken from the upland (vegetables) field, while the contents of the other eight samples were in a narrow range of 40–50 mg kg^{-1}.

Table 3 shows correlation coefficients between heavy metals in their total contents for the nine soils. Among the seven heavy metals, Cr and Ni exhibited the highest correlation coefficient. Zinc showed the significant correlation at 1% level with both Cr and Ni, and correlations between Pb and Cr and between Mn and Zn were significant at 5% level. The significant correlations among Cr, Ni, and Zn were reported by Domingo and Kyuma (1983b) for tropical Asian paddy soils. Cadmium and Cu did not show a significant correlation with any other heavy metals.

Total heavy metal contents of the river-sediment from the Kimnguu River were quite high compared to those of the agricultural soils, except for Mn which was in the same range as for the soils (Table 2). Contents of total Cd, Cr, Cu, Ni, Pb, and Zn were 11.8, 4.9, 5.5, 3.5, 4.0, and 9.5 times higher, respectively, than the average values of the respective heavy metals for the soils.

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

Sample No.	Cd	Cr	Cu	Mn	Ni	Pb	Zn
1	0.16	62.5	73.2	741	33.6	31.9	114.5
2	0.22	72.3	41.3	504	35.3	43.6	106.2
3	0.16	78.9	44.3	378	41.5	43.2	105.8
4	0.23	82.0	50.0	545	45.6	45.1	116.9
5	0.16	65.8	40.1	482	36.6	36.8	98.2
6	0.19	112.8	43.0	750	66.0	45.3	137.2
7	0.36	75.9	43.3	383	40.9	38.6	100.2
8	0.19	68.9	40.1	556	37.2	36.1	105.5
9	0.26	68.9	42.2	451	37.7	36.4	102.6
10	2.48	376	258	719	145.5	157.5	1040

(Oven-dry basis)

Table 3. Correlation coefficients between contents of total heavy metals.

	Cr	Ni	Zn	Pb	Mn	Cd
Ni	0.985**					
Zn	0.828**	0.841**				
Pb	0.731*	0.638	0.462			
Mn	0.359	0.415	0.787*	−0.095		
Cd	0.000	−0.253	−0.477	0.000	0.055	
Cu	−0.251	−0.212	0.242	−0.440	0.557	−0.259

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

Comparison with reference values

Table 4 gives the Vietnam standard for heavy metal contents in soils (Ministry of Science and Environment, 1995) which was recently established to control environmental pollution. Comparison of total Cu, Pb, and Zn contents of agricultural soils (Table 2) with the standard value for the respective heavy metals under the specified pH (Table 6) indicated that none of the soils exceeded the standard values. In contrast to the soils, contents in the river–sediment were extraordinarily over the standard values for Zn and Pb and nearly equal to the standard value for Cu.

Table 5 lists the reported values of total heavy metals in the lithosphere and in soils, quoted from Lindsay (1979), Sposito (1989), and Domingo and Kyuma (1983a). By comparing the data of the present study with the values of Table 5, it was indicated that total heavy metal contents of agricultural soils were all in the common ranges of Cd, Cr, Cu, Mn, Ni, Pb, and Zn for soils. Among these seven heavy metals, contents of Cd, Cr, Mn, and Ni were in the similar magnitude to the selected averages for soils, but contents of other three heavy metals were higher than them. It may indicate the relatively high background levels of Cu, Pb, and Zn in the studied area and probably in the Red River delta area. If compared with the averages for Vietnam (Mekong delta) paddy soils and tropical Asian paddy soils, the contents in the present soils were considerably higher for

Table 4. Standard for heavy metal contents of soils in Vietnam (mg kg^{-1}).

pH	Cu	Pb	Zn	pH	Cu	Pb	Zn
3.5	<15	<20	<20	6.0	<120	<70	<200
4.0	<20	<25	<30	6.2	<180	<75	<300
4.5	<25	<30	<40	6.5	<250	<80	<320
5.0	<40	<40	<60	7.0	260	80	340
5.5	<60	<50	<90	7.5	270	80	360
5.7	<80	<60	<110	8.0	280	80	370

Table 5. Contents of various heavy metals in the lithosphere and soils.

Element	Content in lithosphere (mg kg^{-1})	Common range for soils (mg kg^{-1})	Selected average for soils (mg kg^{-1})			
Cd	0.2	0.01–0.70	0.06	0.35	–	–
Cr	200	1–1000	100	54	137	136
Cu	70	2–100	30	25	23	33
Mn	900	20–3000	600	550	–	–
Ni	100	5–500	40	19	20	22
Pb	16	2–200	10	19	–	–
Zn	80	10–300	50	60	82	66
Reference	1	2	3	4	5	6

1, 2, and 3: Lindsay (1979); 4: Sposito (1989); 5: Domingo and Kyuma (1983a) for Vietnam (Mekong delta) paddy soils; and 6: Domingo and Kyuma (1983a) for tropical Asian paddy soils.

Cu, Ni, and Zn but lower for Cr.

As for the river–sediment, contents of total Cd, Cu, and Zn were remarkably higher than the selected averages for soils and even exceeded the common range for soils. Contents of total Cr, Ni, and Pb were within the common range for soils but considerably over the selected averages for soils. Only total Mn was in the similar magnitude to the selected averages for soils.

Correlation with soil properties

Selected properties of the soil and river–sediment samples are given in Table 6, and correlation coefficients between the soil properties and total heavy metal contents calculated for the nine soil samples are shown in Table 7. Among the seven heavy metals, Cr and Ni showed the highly significant and positive correlation with free Fe_2O_3 oxide and clay contents. The correlation between total Zn and free Fe_2O_3 was also significant at 1% level. Thus variation of total Cr, Ni, and Zn contents of agricultural soils of the studied area can be well explained by the contents of free Fe_2O_3 and/or clay, suggesting that

Table 6. Selected properties of the soil and river–sediment samples.

Sample No.	pH (H_2O)	Organic matter (g kg^{-1})	Clay (<2 μm) (%)	Free Fe_2O_3 (g kg^{-1})	CEC (cmol(+)kg^{-1})
1	7.21	15.9	17.8	22.8	18.0
2	7.26	28.3	21.2	22.7	24.3
3	5.93	30.3	46.4	33.6	20.9
4	6.27	21.9	41.1	32.8	24.4
5	5.72	24.7	29.1	25.8	23.7
6	6.75	30.9	63.4	48.6	27.1
7	5.93	26.0	34.9	26.1	22.6
8	6.47	18.8	29.5	27.7	20.6
9	5.91	22.2	32.2	25.6	24.5
10	6.85	105.0	30.8	43.8	30.7

(Oven–dry basis)

Table 7. Correlation coefficients between total heavy metal contents and selected soil properties.

	pH (H_2O)	Organic matter	Clay (<2 μm)	Free Fe_2O_3	CEC
Cr	0.095	0.640	0.914**	0.954**	0.666*
Ni	0.032	0.549	0.922**	0.968**	0.655
Zn	0.484	0.207	0.646	0.816**	0.375
Pb	0.032	0.766*	0.678*	0.642	0.668*
Mn	0.695*	−0.297	0.144	0.377	0.000
Cd	−0.266	0.084	0.000	−0.176	0.247
Cu	0.494	−0.592	−0.349	−0.215	−0.614

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

artificial contamination or pollution by Cr, Ni, and Zn is negligible or very low. Lead showed the correlation coefficient at 5% level with organic matter and clay contents, and CEC, while Mn showed the significant correlation with pH. It again suggests that the pollution by Pb and Mn is negligible or very low like Cr, Ni, and Zn. According to Domingo and Kyuma (1983b) Cu showed the highly significant correlation with organic matter status. In the present study, however, Cu showed no significant correlation with any of the soil properties. Cadmium also showed no significant correlation with the selected soil properties.

DISCUSSION

Hanoi city has experienced rapid economic development but now is suffered from pollution of water and soils. In order to clarify the pollution of soils in the industrialized and densely–populated area of Hanoi city, soil samples were collected from agricultural soils in Tuliem and Thanhtri districts. Heavy metals were focused on Cd, Cr, Cu, Mn, Ni, Pb, and Zn. Nine soil samples which were collected to cover the whole area with different land uses and land positions were evaluated by the comparison with reference values of total heavy metal contents for soils and the correlation with selected soil properties. However, they did not show any indication of artificial contamination or pollution by heavy metals, since total heavy metal contents were below the Vietnam standard for heavy metal contents in soils and within the common range and around the selected averages for soils. In addition, total heavy metal contents were significantly correlated with one or more than two of the selected soil properties.

One possible pollution was indicated for Cu of the upland field where vegetables are cultivated throughout the year. Total Cu content at the field did not exceed the Vietnam standard for Cu in soils and was within the common range for soils, but higher by 20–30 mg kg^{-1} than the total Cu contents of the other eight soil samples which showed the quite similar contents with one another. In the vegetable field around the sampling site, farmers conveniently apply a lot of pesticide to keep growth and production of vegetables. Total Cu content of the vegetable field is below the critical level but would be over that level in near future by continuation of heavy application of pesticide.

In contrast to the agricultural soils, the river–sediment which was collected from the Kimngun River showed the quite high contents of heavy metals, except for Mn, with an indication of their accumulation in the river bed. The most heavy accumulation was indicated for Zn. Total Zn content of the river–sediment was about 1,000 mg kg^{-1} which was remarkably over the Vietnam standard for Zn in soils and exceeded the common range for soils. Total Cd content of the river–sediment was 2.48 mg kg^{-1} and exceeded the common range for soils. Following Zn and Cd, considerable accumulation of Cr, Cu, Ni, and Pb was noticed. Severe pollution by different heavy metals was indicated for the river–sediment, and discharge of industrial wastes from many factories along the river can be suggested as a main source of the heavy metal accumulation, but only for one site. More river–sediment samples should be collected from different rivers of the area and measured for total heavy metals to identify the magnitude and extension of heavy metal pollution in the river bed of Tuliem and Thanhtri districts as a future work.

In the Red River delta area, farmers have for a long time used mud of rivers and canals as a organic amendment or fertilizer to keep soil fertility. Accumulation of heavy metals in the river–sediment is probably a recent occurrence, even if it is a real matter. However, continuation of application of the river–sediment to the surface of agricultural field would become a probable source of soil pollution by heavy metals.

CONCLUSIONS

Pollution of agricultural soils by heavy metals at Tuliem and Thanhtri districts was not indicated except for Cu at one upland field. Total Cu content of that field was higher by 20–30 mg kg^{-1} than those of the other fields, although it was below the critical level of the Vietnam standard. These districts have been rapidly industrialized and populated in Hanoi, but pollution of agricultural soils by heavy metals is limited and very low up to the present.

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