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Interaction Between Heavy Metals and Nitrogen Fertilizers Applied to Soil-Vegetable Systems

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In China, application of chemical fertilizers has been expanded rapidly in recent years in order to increase per unit output of agricultural production, in particular, under conditions of the "big-cote" planting (Li *et al.*, 2000). On the one hand, the content of nitrate in agricultural products is going beyond its national food-safety standard due to superfluous application of nitrogen fertilizers (AEMSC, 2001); and on the other hand, long-term application of low-quality phosphorus fertilizers has resulted in pollution of Cd in more and more agricultural soils (Li, 2001; Sun *et al.*, 2001). Pollution of Pb in agricultural soils is being aggravated by dry and wet precipitation (He *et al.*, 1998). According to AEMSC (2001), the area of agricultural land polluted by heavy metals such as Cd, Pb, As, Cu and Zn has reached 2.0×10^7 ha, and concentrations of heavy metals in more than 1.0×10^7 tons of foodstuffs have annually exceeded their national food-safety standards. It was estimated by AEMSC (2001) that the direct economic loss resulting from pollution of foodstuffs by heavy metals has risen to 2.2×10^{10} Yuan RMB.

It can be clearly understood that a great deal of nitrate in agricultural products is derived from superfluous application of nitrogen fertilizers to agricultural soils (Li *et al.*, 2000; Yan and Zhu, 2000; Zhou and Huang, 2001). Relationships between accumulation of heavy metals in crops and pollution of heavy metals in soils have been well documented (Pokorny and Ribaric-Lasnik, 2000; Sun *et al.*, 2001; Syakalima *et al.*, 2001; Tungare and Sawant, 2002). However, whether the increase in heavy metals accumulated in agricultural products is related to the superfluous application of chemical fertilizers is a question still to be answered.

MATERIALS AND METHODS

Surface red soil samples contaminated by heavy metals such as Pb and Cd were collected from 0-20 cm of five vegetable fields near a brick and cement plant and a highway in the suburbs of Jinhua City, Zhejiang Province, China, using a 5-point quincunx sampling method (Zhou, 1996). In a relatively clean location, at

Table 1. Basic properties and heavy metal concentrations of the tested soils.

Soil type	pH	Organic matter (%)	Clay content < 0.002 mm (%)	Total nutrient (%)			Heavy metal (mg kg^{-1})	
				N	P	K	Pb	Cd
Red soil	5.91	1.01	48.16	0.13	0.16	0.91	32.8	0.21
Polluted red soil	6.14	0.96	46.86	0.29	0.18	0.94	154.3	0.38

least 1000 m from each contaminant vegetable field, normal surface red soil samples were collected. In other words, there were 5 replicates of contaminant and clean soil samples, respectively. The same type of the soil samples from the five sites (namely 5 replicates) were thoroughly mixed with normal manual method before chemical analyses and pot-culture experiments (Zhou and Sun, 2002).

After the mixed contaminant and clean soil sub-samples were respectively air-dried and ground, pH (soil/water ratio = 1:1), organic matter, clay content, total nitrogen, total phosphorus and total potassium in the two tested soils were determined according to the methods which were recommended and depicted by NAU (1996) and Hong (1987). The basic properties of the two tested soils are listed in Table 1. Partially air-dried and ground samples were analyzed for total Cd, Pb, Cu and Zn using the atomic absorption spectrophotometer (180-80 type, made in Japan) after a wet digestion of the air-dried samples with the mixture of HNO_3 and $HClO_4$ (He *et al.*, 1998; Sun *et al.*, 2001). The initial concentrations of Pb and Cd in the two tested soils are also listed in Table 1.

After the relatively clean soil samples were mixed with various doses of NH_4NO_3 (a nitrogen fertilizer), Cd and Pb (Table 2) and the polluted soil samples were only mixed with various doses of NH_4NO_3, all the freshly mixed topsoil samples were put into pots marked with numbers. After the mixture, the concentration of NH_4NO_3 in the polluted soil was 0, 5, 10, 20, 40, 80 and 160 mg kg^{-1} dw soil, respectively. All treatments were replicated four times, and each replication consisted of 4.39 kg of fresh red soil, amounting to 4.00 kg of air-dried soil samples for each replicate. After tap water was added to the soils, fifteen seeds of radish (*Raphanus sativus* L) and carrot (*Daucus carota* L varsativa DC) and five seeds of potato (*Solanumtuberosum* L) were then sown in each pot. Avoiding waterlogging, drought and insect pests with manual methods was the key step of the pot-culture experiment.

After mature vegetables were harvested, edible parts were washed with a nonionic detergent, rinsed with tap water, drip-dried and weighed. The drip-dried samples

Table 2. Concentrations (mg kg^{-1}) of Cd, Pb and NH_4NO_3 in clean soil samples after treatments.

Treatment	Number of treatments				
	1	2	3	4	5
Added Cd	0.0	0.0	0.0	3.0	3.0
Added Pb	0.0	0.0	100.0	0.0	100.0
Added NH_4NO_3	0.0	160.0	160.0	160.0	160.0

regarded as fresh weight were ground, digested with a mixture of concentrated HNO_3 and 1:1 HS_2O_4 solution, and analyzed for Cd, Pb, Cu and Zn using the atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The accumulation of Cd in edible parts of radish, carrot and potato had obviously increased (Table 3) due to single high-dose application of the nitrogen fertilizer (treatment 2), 1.5-1.8 times that under the control condition without the addition of the nitrogen fertilizer (treatment 1). The simultaneous addition of Pb and the nitrogen fertilizer to the soil (treatment 2) also promoted the absorption of Cd by the three crops. However, the average concentration of Cd in the three crops in treatment 2 was not markedly higher that in treatment 1. In other words, increased Cd accumulation in the crops could be induced by action of the nitrogen fertilizer other than interaction between Pb and the nitrogen fertilizer. This was further demonstrated by comparing treatment 5 with treatment 4: the absorption of Cd by the three crops in treatment 5 was slightly high in comparison with that in treatment 4.

There were significantly positive relationships between the accumulation of Cd in the three crops growing on the polluted soil and the dosage of the nitrogen fertilizer applied to the polluted soil (Figure 1). The relationships can be expressed by following regression equations:

$$Y_{Cd}(\text{Radish}) = 1.2 \times 10^{-3}X + 0.218 \quad (R^2=0.460, n=28, p<0.005) \quad (1)$$
$$Y_{Cd}(\text{Carrot}) = 8.0 \times 10^{-4}X + 0.177 \quad (R^2=0.361, n=28, p<0.005) \quad (2)$$
$$Y_{Cd}(\text{Potato}) = 1.6 \times 10^{-3}X + 0.261 \quad (R^2=0.537, n=28, p<0.005) \quad (3)$$

Where Y_{Cd}(Radish), Y_{Cd}(Carrot) and Y_{Cd}(Potato) are the concentration (mg kg^{-1}) of Cd in radish, carrot and potato growing on the polluted soil, respectively; X is the concentration of NH_4NO_3 added to the polluted soil; R is the correlation coefficient; n is number of treatments; and p is the significance level.

Table 3. Concentrations (mg kg^{-1}) of Cd in crops growing in clean soil fortified with various exposed concentrations of Cd, Pb and NH_4NO_3.

Treatment	Accumulated Pb	Crop type		
		Radish	Carrot	Potato
1	Mean	0.16	0.14	0.24
	SD	0.067	0.030	0.056
2	Mean	0.29	0.21	0.37
	SD	0.070	0.049	0.046
3	Mean	0.28	0.23	0.40
	SD	0.041	0.037	0.039
4	Mean	0.77	0.60	1.07
	SD	0.143	0.152	0.160
5	Mean	0.81	0.69	1.18
	SD	0.124	0.191	0.193

The high-dose application of the nitrogen fertilizer had an influence on the accumulation of Pb in edible parts of radish, carrot and potato (Table 4). The average concentration of Pb in the three crops growing on all the soils treated by NH_4NO_3 was higher than that under the control condition without the addition of NH_4NO_3 (treatment 1). By comparing treatment 4 with treatment 2 and comparing treatment 5 with 3, it was shown that interaction between Cd and the nitrogen fertilizer could further promote the accumulation of Pb in edible parts of the three crops.

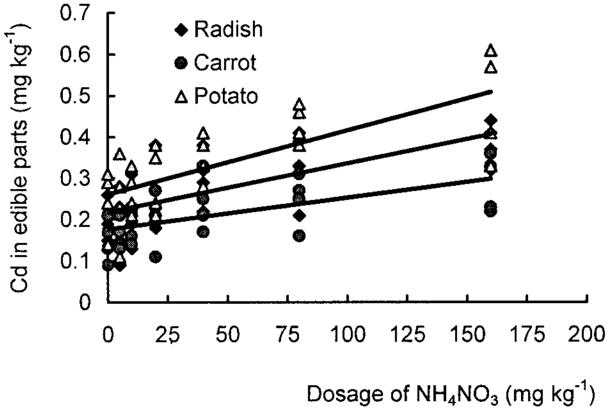

Figure 1. Relationship between the accumulation of Cd in edible parts of radish, carrot and potato, growing on polluted soil, and the amount of applied nitrogen fertilizer

Table 4. Concentrations (mg kg^{-1}) of Pb in crops growing in clean soil fortified with various exposed concentrations of Cd, Pb and NH_4NO_3.

Treatment	Accumulated	Crop type		
	Pb	Radish	Carrot	Potato
1	Mean	0.14	0.17	0.09
	SD	0.025	0.042	0.039
2	Mean	0.23	0.28	0.20
	SD	0.063	0.070	0.074
3	Mean	3.93	5.73	3.12
	SD	1.146	0.832	1.061
4	Mean	0.32	0.39	0.30
	SD	0.072	0.106	0.074
5	Mean	4.91	7.39	4.51
	SD	0.601	0.804	0.976

Figure 2 shown that the concentration of Pb accumulated in edible parts of the three crops growing on the polluted soil gradually increased with the amount of nitrogen fertilizer applied to the polluted soil. The positive relationships can be expressed by following regression equations:

$$Y_{Pb}(\text{Radish}) = 5.5 \times 10^{-3}X + 0.903 \quad (R^2=0.795, n=28, p<0.005) \quad (4)$$
$$Y_{Pb}(\text{Carrot}) = 6.2 \times 10^{-3}X + 1.469 \quad (R^2=0.823, n=28, p<0.005) \quad (5)$$
$$Y_{Pb}(\text{Potato}) = 6.5 \times 10^{-3}X + 0.911 \quad (R^2=0.831, n=28, p<0.005) \quad (6)$$

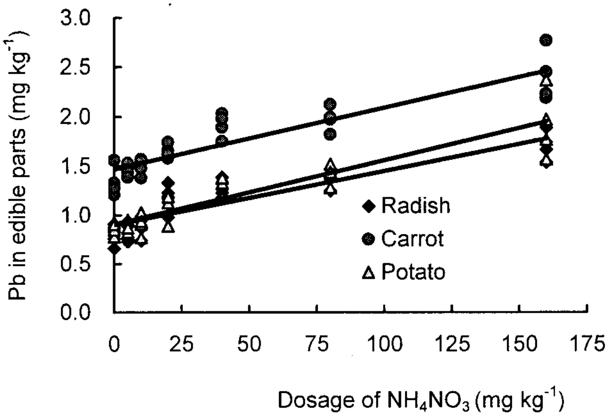

Figure 2. Relationship between the accumulation of Pb in edible parts of radish, carrot and potato, growing on polluted soil, and the amount of applied nitrogen fertilizer

Where Y_{Pb}(Radish), Y_{Pb}(Carrot) and Y_{Pb}(Potato) are the concentrations (mg kg^{-1}) of Pb in radish, carrot and potato, growing on the polluted soil, respectively.

High-dosage application of the nitrogen fertilizer to agricultural soils could increase the accumulation of some heavy metals such as Cd and Pb in agricultural products, thus increasing the potential ecological risk of excessive chemical fertilizer application.

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