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Chemical speciation of cadmium and lead and their bioavailability to cole (*Brassica campestris* L.) from multi-metals contaminated soil in northwestern China

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ABSTRACT

A pot experiment was conducted to study the relationship between speciation distribution of cadmium (Cd) and lead (Pb) and their availability to cole (*Brassica campestris* L.) grown on the Cd–Pb polluted soil in northwest of China. The results showed that Cd in the unpolluted soil was mainly bound to carbonate fraction (F2) and Fe–Mn oxide fraction (F3), and Pb was mainly bound to carbonate fraction (F2) and residual fraction (F5). However, marked change of Cd and Pb fractionation was observed with increasing soil Cd and Pb concentrations, where the concentrations of Cd in F1 (exchangeable fraction), F2 and F3 increased significantly ($p < 0.001$ for F1, F2 and F3), and Pb in F1, F2, F3 and F4 increased significantly ($p < 0.001$ for F1, F2, F3 and F4). The correlation analysis between the fraction distribution coefficient of Cd and Pb in the soil and Cd and Pb concentration accumulated in cole showed that both Cd and Pb in F1 fraction in the soil made the greatest contribution on the accumulation of Cd and Pb in cole. Higher bio-concentration factors (BCFs) and translocation factors (TFs) for Cd and lower BCFs and TFs for Pb were observed in the cole, respectively. Cd had higher accumulation in the edible parts of the cole, but Pb had lower accumulation in that. Therefore, Cd has higher risk to human health than Pb when people eat the coles grown in Cd–Pb polluted soil in northwestern China.

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Introduction

Heavy metal contamination of soils coming from industry or agriculture, such as smelting industries, residues from metalliferous mined, pesticide, fertilizers, municipal compost, is one of the major environmental problems in the world.[1–10] Excessive metal concentrations in the contaminated soils can result in soil quality degradation, crop yield reduction, and poor quality of agriculture products.[11,12] The subsequently transferred and accumulated heavy metals in human beings' bodies through food chain might be a threat to health.[13–15]

Several studies have suggested that the toxicity and mobility of heavy metals depends not only on their total amounts but also on their chemical fractionation in soil.[16–25] There are many classification methods to assess the chemical fractions of heavy metals in soil. [20,26–28] Tessier's five-step sequential extraction method has been widely used, in which heavy metals in soils are categorized in the five fractions: exchangeable fraction (F1), carbonate fraction (F2), Fe–Mn oxide fraction (F3), organic matter fraction (F4) and residual fraction (F5). [20,25,26,29] F1 is bioavailable fractionation; F2, F3 and F4 are potential bioavailable fractionations; F5 is unbioavailable fractionation.[16,25,30]

In recent decades, some vegetable fields have been irrigated with wastewater from the industry and agriculture activities in the arid area and therefore have been heavily polluted by heavy metals, especially by cadmium (Cd) and lead (Pb) in northwestern China,[13,31] which caused a threat to human health. According to reported literature, about 1000 ha of agricultural soils have been polluted with Cd and Pb in Baiyin city of northwestern China.[31,32] In general, many heavy metals including Cd and Pb are nonessential elements with biological toxicity. In order to avoid the pollution of the food chain by Cd and Pb, it is essential to assess their bioavailability in soil.[33] Many studies have indicated that the uptake of heavy metals by plants was related not only to the physical and chemical properties of soils and soil types but also plant species.[34–36]

Some studies [37–40] have reported chemical speciations of Cd and Pb and their bioavailability to cole grown in polluted cinnamon soil and oasis soil of China and found that Cd and Pb in both F2 and F3 in the soil made the greatest contribution on the accumulation of Cd and Pb in cole, and Cd had higher accumulation than Pb in the edible parts of the cole. Yang et al.[14,15] also have reported chemical speciation and bioavailability of Cd

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in oasis soil, bioaccumulation and translocation of Cd in cole grown in the Cd-polluted oasis soil in northwestern China. Their findings showed that Cd in F1 in the oasis soil made the greatest contribution on the accumulation of Cd in cole, and Cd had higher accumulation in the edible parts of the cole. But there was almost not reported that bioavailability of heavy metals to cole in gray calcium soil in northwestern China.

As vegetable consumed for their edible parts, cole (*Brassica campestris* L.) has been widely cultivated in northwestern China where individual consumption figures for the cole by the local population is approximately 0.30 kg average per person per day,[41] People who consume cole grown in Cd–Pb polluted soils in the area are at risk of an elevated Cd and Pb exposure. The proposed work was aimed to study the speciation of Cd and Pb and their bioavailability to cole grown in the Cd–Pb polluted gray calcium soil in northwestern China using pot experiments. Human health risk from Cd and Pb in cole was also evaluated.

Materials and methods

Experimental design

Experimental reagents were selected with superior grade (Tianjin Kermel Chemical Reagents Corporation, China) and certified reference material samples, GSS-1 (GBW07401) and GSB-6 (GBW10015) were used. The two parameters bio-concentration factor (BCF) and the translocation factor (TF) were calculated. BCF was the ratio of the metal concentration in plant tissues to that in their rooted soils,[24,42,43] and TF was the ratio of metal concentration in other plant parts to that in roots.[24,43]

Pot experiments were conducted under open air conditions in April 2015 at Baiyin city in northwestern China. This area belongs to a semi-arid region with low precipitation (180–450 mm annually), high evapotranspiration (1500–1600 mm annually), and high temperatures in the summer (22 °C). The soils which belong to gray calcium soil are derived from the suburb of Baiyin city, and textures are mainly clay loam. Other soil properties are as follows: pH (in H₂O) 7.80, organic matter content 12.59 g kg⁻¹, CaCO₃ content 5.28%, and cation exchange capacity 8.82 cmol kg⁻¹. The background concentration levels of Cd and Pb in the soil are 0.12 and 18.20 mg kg⁻¹ dry weight (dw), respectively in northwestern China.[31]

The soil used was gray calcium soil, excavated from a vegetable field at 0–20 cm depth with spade, and sub-samples collected were mixed to obtain a composite sample in accordance with the standard method.[44] The soil sample was air dried and ground, then passed through a 10 mm sieve to remove large stones and grass debris. Nine treatments (one control and eight amendments) were replicated three times in a randomized block design. The control was not amended with inorganic Cd and Pb. The others, one by one, were

spiked with different solutions of compound cadmium nitrate and lead nitrate and single cadmium nitrate or lead nitrate to elevate soil, respectively. Cd and Pb concentrations as follows: 0.35, 0.75, 1.25, 1.80, 2.50, 3.50, 5.00, and 7.50 mg kg⁻¹ dw for Cd, and 75, 150, 230, 320, 450, 700, 1000, and 1350 mg kg⁻¹ dw for Pb, which was designed based on our field pollution investigation in the Cd–Pb polluted soil.[13] The heavy metal was added by spraying a solution of metal salt over relatively dry soil spread out on a large tray. The soil was turned over and sprayed several times, and watered and left for equilibration outdoors for four weeks, then 2.5 kg soil was transferred to each plastic pot (20 cm in diameter and 15 cm in height) before planting coles. The cole plants were seeded directly into the soil in the pots, and two weeks after sowing, the number of seedlings was thinned to four per pot for cole. During the experimental period, tap water was added to compensate for evaporation and transpiration and soil moisture content was maintained at approximately 60% of water holding capacity.

Whole plants were harvested after 60 days of growth and cut with scissors into separate parts grown under and above the soil. Shoots (leaves + stems) were washed three times using de-ionized water. Roots were washed thoroughly with tap water to eliminate soil particles, and rinsed three times with de-ionized water. Then the fresh weight (fw) of roots and shoots were recorded. Roots and shoots were dried in an oven at 70 °C to constant weight. The oven-dried samples were ground with a stainless steel grinder (FW-100, China), passed through 2 mm nylon sieve for further experiment.

Composite soil samples were collected from the pots after harvesting the coles, air-dried at room temperature, ground with pestle and mortar, passed through 100 mesh ($\phi = 0.149$ mm) nylon sieve.

Plant samples and soil samples were stored in plastic bottles, respectively, before analyses.

Determination of Cd and Pb in soils and coles

Total Cd and Pb concentrations in soils were determined according to national standards of China.[45] Total Cd and Pb in cole were extracted using the acid digestion mixture (HNO₃–HClO₄–HF).[46,47] The clear solution obtained from the digestion was filtered and reconstituted to the desired volume for analysis using an atomic absorption spectrometer (AAS, M6MK2, Thermo Electron Corporation, USA).

Determination of Cd and Pb fractionation in soil using Tessier's sequential extractions

Tessier's sequential extraction procedure was used in this experiment. Cd and Pb were extracted by MgCl₂ solution in F1; by HAC–NaAc solution in F2; by NH₂OH·HCl solution in F3; by HNO₃–H₂O₂–NH₄Ac solution in F4; and

by $\text{HNO}_3\text{-HClO}_4\text{-HF}$ solution in F5.[26] Cd and Pb in soil solutions obtained from Tessier's sequential extraction procedure were also determined by an atomic absorption spectrometer (AAS, M6MK2, Thermo Electron Corporation, USA).

Quality assurance of data generation

Replicates, blanks and certified reference materials, GSS-1 (GBW07401) and GSB-6 (GBW10015), were included for quality assurance. The total and various speciation Cd and Pb concentrations in soils and plants were determined in triplicate, and the coefficient of variation ranged between 5 and 10% in triplicate analysis. The percentage recovery from certified reference materials were from 90 to 110% throughout the analysis procedures.

Statistical analysis

The means and standard deviations (SD) were calculated by Excel2003 for windows. One-way analysis of variance was carried out with SPSS16.0. The significant ($p < 0.05$) difference observed between treatments and multiple comparisons were made by the LSD test.

Results and discussion

Chemical fractions of Cd and Pb in the soil

The experiment results in Figure 1 showed that with increasing Cd and Pb concentrations in soils, the concentrations of both Cd and Pb in exchangeable fraction (F1), carbonate fraction (F2) and Fe–Mn oxide fraction (F3) increased significantly ($p < 0.01$ for F1, F2 and F3) probably because of the addition of Cd and Pb in the form of solution, which was highly bioavailable. The parameter fraction distribution coefficient (FDC) usually was defined as the percentage of the each heavy metal fraction, and the FDCs of Cd and Pb increased

significantly in F1 and F2 ($p < 0.01$) with increasing soil Cd and Pb concentration, however reduced significantly in F5 ($p < 0.01$) (Figure 2). And the FDCs of Cd in F1 were much higher than Pb because of greater mobility of Cd in the soil.[13]

F5 comprises primary and secondary minerals within the crystal structure that is unlikely to be released in the mid- and long-term under the conditions normally found in nature. Previous studies have shown that in unpolluted soils, F5 was the main heavy metals fraction which was not bio-available for the plants,[1,48,49] but the percentage of heavy metals associated with available fraction increased with the increase of total heavy metals in the growth medium.[1,29,48–50] Bose et al.[51] reported that Cd was bound with F3 in unpolluted garden soil in India. Similar results were observed in present study. The results suggested that the fraction of both Cd and Pb in unpolluted soil was mainly in F3, however, the bio-available fraction concentration increased significantly ($p < 0.01$), and the percentage of Cd and Pb associated with F5 decreased significantly ($p < 0.01$) with increased soil Cd and Pb concentrations.

Effects of Cd and Pb stress on cole growth

The fresh weight and Cd and Pb concentrations of roots and shoots of cole grown with different Cd and Pb treatments are listed in Table 1.

The fresh biomass of cole roots and shoots generally increased at first, and reached peak values, then decreased with increased soil Cd and Pb concentrations (Table 1). When the treatment level was T3 (1.25 mg kg⁻¹ of Cd and 230 mg kg⁻¹ of Pb), the fresh biomass of cole reached the maximum value (4.20 ± 0.46 g pot⁻¹ for root and 105.45 ± 9.55 for shoot, respectively), increased by 21.38 and 23.05%, respectively, compared with the control, indicating that this level was hazardous threshold of cole, and beyond it, the growth of cole would be inhibited.

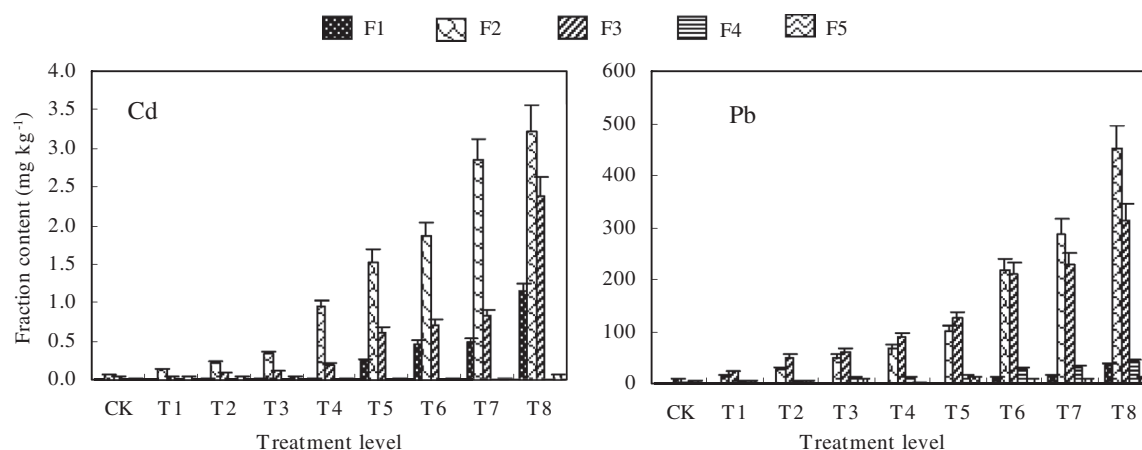


Figure 1. Distribution of the concentration of Cd and Pb fractions in the soil, respectively. Note: F1: exchangeable fraction, F2: carbonate fraction, F3: Fe–Mn oxide fraction, F4: organic matter fraction, F5: residual fraction. Values are means ± SD of three replicates.

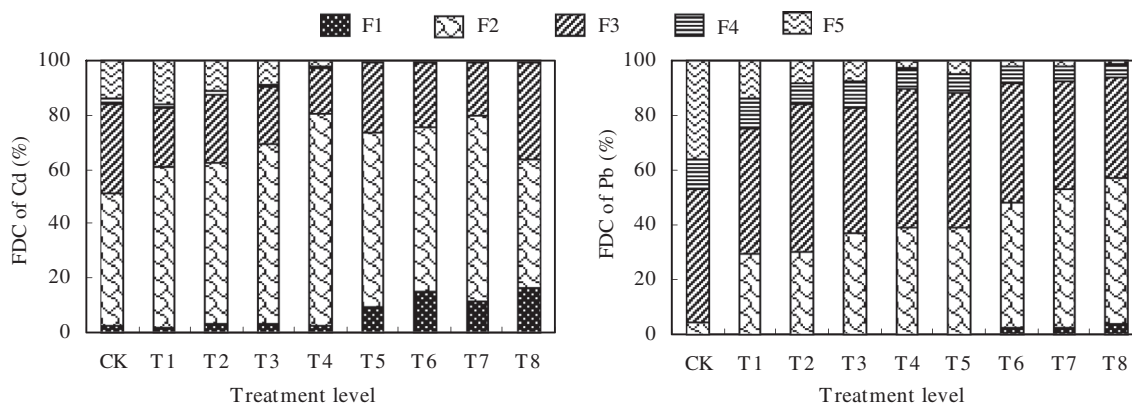


Figure 2. Distribution of the fraction distribution coefficient (FDC) of Cd and Pb in the soil, respectively. Note: Values are means of three replicates.

Table 1. Change of fresh weight and heavy metals content in cole under Cd–Pb compound treatment.

Treatment level (Cd + Pb mg kg ⁻¹)	Fresh weight (g pot ⁻¹)		Cd concentration (mg kg ⁻¹)		Pb concentration (mg kg ⁻¹)	
	Root	Shoot	Root	Shoot	Root	Shoot
CK (Cd 0 + Pb 0)	3.46 ± 0.35a	85.70 ± 8.37a	0.10 ± 0.01a	0.17 ± 0.01a	0.85 ± 0.05a	0.06 ± 0.00a
T1 (Cd 0.35 + Pb 75)	3.69 ± 0.39a	96.02 ± 9.20b	0.11 ± 0.01a	0.23 ± 0.02a	1.91 ± 0.23b	0.06 ± 0.00a
T2 (Cd 0.75 + Pb 150)	3.58 ± 0.36a	75.37 ± 7.35c	0.22 ± 0.02b	0.52 ± 0.03b	3.35 ± 0.30c	0.08 ± 0.00a
T3 (Cd 1.25 + Pb 230)	4.20 ± 0.46b	105.45 ± 9.55d	0.35 ± 0.02b	0.86 ± 0.04b	5.70 ± 0.35d	0.11 ± 0.01a
T4 (Cd 1.80 + Pb 320)	2.62 ± 0.26c	81.05 ± 8.26a	0.58 ± 0.03c	1.41 ± 0.10c	11.02 ± 1.11e	0.90 ± 0.05b
T5 (Cd 2.50 + Pb 450)	3.23 ± 0.33a	90.13 ± 9.31b	0.93 ± 0.05c	1.94 ± 0.18c	11.86 ± 1.10e	0.88 ± 0.06b
T6 (Cd 3.50 + Pb 700)	2.54 ± 0.15c	74.88 ± 7.45c	1.39 ± 0.14d	3.35 ± 0.33d	20.08 ± 1.20f	1.79 ± 0.12c
T7 (Cd 5.00 + Pb 1000)	2.93 ± 0.21c	85.25 ± 8.35a	1.61 ± 0.16d	3.48 ± 0.35d	31.16 ± 2.31g	1.83 ± 0.15c
T8 (Cd 7.50 + Pb 1350)	2.70 ± 0.26c	79.70 ± 7.90c	2.50 ± 0.25e	4.99 ± 0.40e	52.07 ± 5.20h	3.61 ± 0.35d

Notes: Values are presented as mean ± SD of three replicates. One-way ANOVA (1 factor: different Cd and Pb treatments) was performed for each parameter on Cd and Pb concentration. Data in the same column followed by different letters are significantly different from each other ($p < 0.05$) according to the LSD test.

Some studies [38,39,52] have reported that dried weight of cole increased at first, then decreased under soil Cd and Pb stress. This conclusion was in agreement with the present studies. These results indicated that the toxic effect of Cd and Pb on cole had threshold values. Cole growth could be enhanced by lower concentrations of Cd and Pb (≤ 1.25 mg kg⁻¹ of Cd and 230 mg kg⁻¹ of Pb), but inhibited by higher concentrations. This may be attributed to high concentrations of Cd and Pb that damaged cole roots, [42,52] and inhibited uptake of nutrient elements in roots, then inhibited the growth of cole.

Bioaccumulation of Cd and Pb in cole

The amounts and distribution of Cd and Pb accumulated in cole under various treatments are shown in Table 1. Both Cd and Pb concentrations in cole increased significantly ($p < 0.01$) with increased soil Cd and Pb concentrations. Compared with the control, Cd concentrations of cole root and shoot increased by 24.00-fold and 28.35-fold, respectively, and Pb concentrations increased by 60.26-fold and 59.17-fold, respectively at the treatment level was T8 (7.50 mg kg⁻¹ of Cd and 1350 mg kg⁻¹ of Pb) in the soil.

According to the China Environmental Quality Standard for Soils, [53] Cd and Pb limits for the soils

used for cole production are 0.6 and 350 mg kg⁻¹, respectively where soil pH > 7.5. At Cd and Pb level of 0.6 and 350 mg kg⁻¹, respectively in soil, Cd and Pb concentrations in cole shoot were 0.24 mg kg⁻¹ (calculated by statistical regression equation $y = 0.6803x + 0.1692$, $R^2 = 0.965$, $p < 0.001$, where y is Cd concentration in cole, x is the concentration of Cd in soil) and 0.70 mg kg⁻¹ (calculated by $y = 0.0025x - 0.1763$, $R^2 = 0.940$, $p < 0.001$), respectively. At this level of Cd and Pb addition, the national allowable limits of Cd and Pb in cole were all exceeded, compared with maximum levels of contaminants in cole foods, 0.2 mg kg⁻¹ of Cd and 0.3 mg kg⁻¹ of Pb. [54] However, the previous studies [42,55] found the bioavailability of Cd and Pb was much lower in the field contaminated soil than in the artificially contaminated soil used in the pot experiment, therefore, Cd and Pb concentrations in vegetables was much higher in the pot experiment than in the field trial.

In general, cole accumulated higher Cd concentrations in its edible parts than Pb, which was in agreement with previous studies. [38–40] Xu et al. [56] found that NaCl extractable Cd (Cd-binding protein) predominates in vegetable roots, and acetic acid extractable Pb (lead hydrogen phosphate and lead phosphate) and HCl extractable Pb (lead oxalate) are the main forms in those, therefore, Cd is more easy to migrate from vegetable roots to shoots.

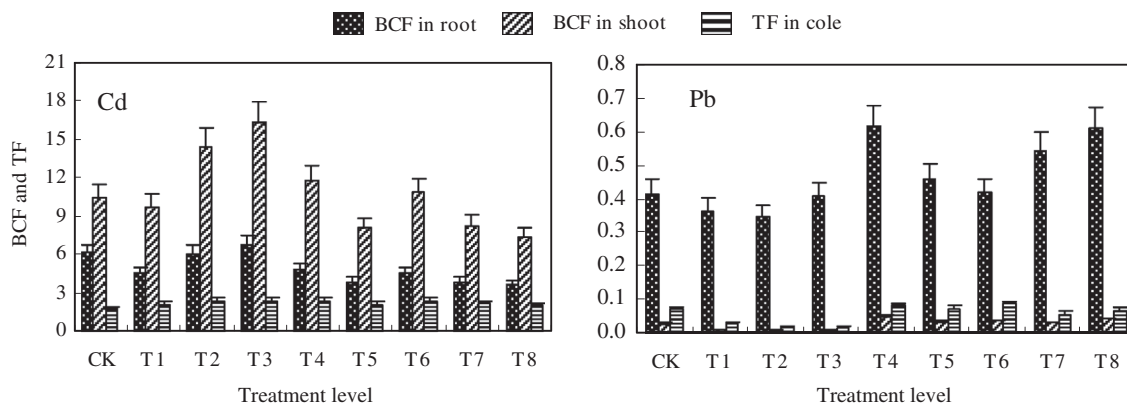


Figure 3. Change of bio-concentration factor (BCF) and the translocation factor (TF) of Cd and Pb with treated level. Note: Values are means \pm SD of three replicates.

The present study found the order of Cd accumulation in cole was shoot > root, while Pb was root > shoot (Table 1). Similar results were observed in the previous studies.[38–40]

The BCF of Cd and Pb in cole roots and shoots under various treatments are shown in Figure 3. The BCF values of Cd were ranged from 3.66–6.74 for roots, 7.31–16.30 for shoots, respectively; those of Pb 0.35–0.62 for roots, 0.01–0.05 for shoots, respectively. Compared with the oasis soil (pH 8.47), [14,15] the BCF values of Cd in cole grown on gray calcium soil (pH 7.80) were bigger probably due to the different soil type, which showed Cd is easier to migrate from soil to cole grown on gray calcium soil than oasis soil. In general, the BCFs for Cd in cole were higher than Pb ($p < 0.01$). Similar results were observed in the previous studies.[37–40,57]

Sun et al. [35] found that the cumulative coefficients of heavy metals were higher in cole plants under low heavy metal doses, on the contrary, the cumulative coefficients of heavy metals were low under high doses, but the absolute amount of heavy metals accumulated increased with the increased heavy metal doses. Similar result was observed in the present study, the BCFs of Cd and Pb in cole increased, reached a maximum value, then decreased with increasing soil Cd and Pb concentrations (Figure 3).

The TFs of Cd and Pb in cole under various treatments were ranged from 1.69–2.42 and 0.02–0.09, respectively (Figure 3). Compared with the oasis soil (pH 8.47), [14,15]

the TF values of Cd in cole grown on gray calcium soil (pH 7.80) were bigger probably due to the different soil type, which showed Cd is easier to migrate from cole roots to shoots grown on gray calcium soil than oasis soil. In general, the TFs of Cd in cole were much higher than Pb, suggesting that Cd had greater mobility than Pb towards uptake by cole. This conclusion was in agreement with Wang et al. [38].

The above-mentioned results showed that the BCF and TF of Cd and Pb in cole had threshold values, beyond which, the roots of cole may be damaged by Cd and Pb, although the uptake and accumulation of Cd and Pb in cole was continuing, but their uptake rates gradually reduced, hence the BCFs of Cd and Pb in cole increased at first, then decreased. The above results also suggested that cole accumulated higher Cd concentrations than Pb in its edible parts grown in the polluted soil. Therefore, Cd in cole grown in the Cd–Pb polluted soil and consumed by humans has higher risk to human health than Pb.

Interaction between Cd and Pb in soil and cole

Concentrations of both Cd and Pb in cole under Cd–Pb compound contamination (Tables 1) were lower than those under single Cd or Pb contamination (Table 2), which indicated that there was antagonistic effect between Cd and Pb in soil under Cd–Pb compound pollution.

Table 2. Concentration of Cd and Pb in cole with single Cd or Pb treatment.

Treatment level (Cd/Pb mg kg ⁻¹)	Cd concentration (mg kg ⁻¹ fw)		Pb concentration (mg kg ⁻¹ fw)	
	Root	Shoot	Root	Shoot
CK (Cd 0/Pb 0)	0.01 \pm 0.00a	0.09 \pm 0.00a	3.43 \pm 0.32a	3.33 \pm 0.30a
T1 (Cd 0.35/Pb 75)	0.19 \pm 0.02b	0.42 \pm 0.03b	10.44 \pm 0.95b	2.37 \pm 0.21b
T2 (Cd 0.75/Pb 150)	0.26 \pm 0.02b	0.84 \pm 0.08b	18.46 \pm 1.75c	3.30 \pm 0.30a
T3 (Cd 1.25/Pb 230)	1.14 \pm 0.10c	1.53 \pm 0.14c	28.32 \pm 2.80d	4.03 \pm 0.35a
T4 (Cd 1.80/Pb 320)	1.42 \pm 0.12c	1.76 \pm 0.15c	37.88 \pm 3.66e	5.01 \pm 0.48c
T5 (Cd 2.50/Pb 450)	2.28 \pm 0.20d	3.32 \pm 0.30d	53.11 \pm 5.12f	6.07 \pm 0.55d
T6 (Cd 3.50/Pb 700)	2.34 \pm 0.22d	3.35 \pm 0.33d	83.09 \pm 8.23 g	8.58 \pm 0.72e
T7 (Cd 5.00/Pb 1000)	3.08 \pm 0.28e	3.64 \pm 0.31d	135.77 \pm 12.25 h	16.96 \pm 1.58f
T8 (Cd 7.50/Pb 1350)	4.70 \pm 0.43f	4.53 \pm 0.40e	186.18 \pm 15.33i	18.81 \pm 1.88f

Notes: Values are presented as mean \pm SD of three replicates. One-way ANOVA (1 factor: different Cd or Pb treatments) was performed for each parameter on Cd or Pb concentration. Data in the same column followed by different letters are significantly different from each other ($p < 0.05$) according to the LSD test.

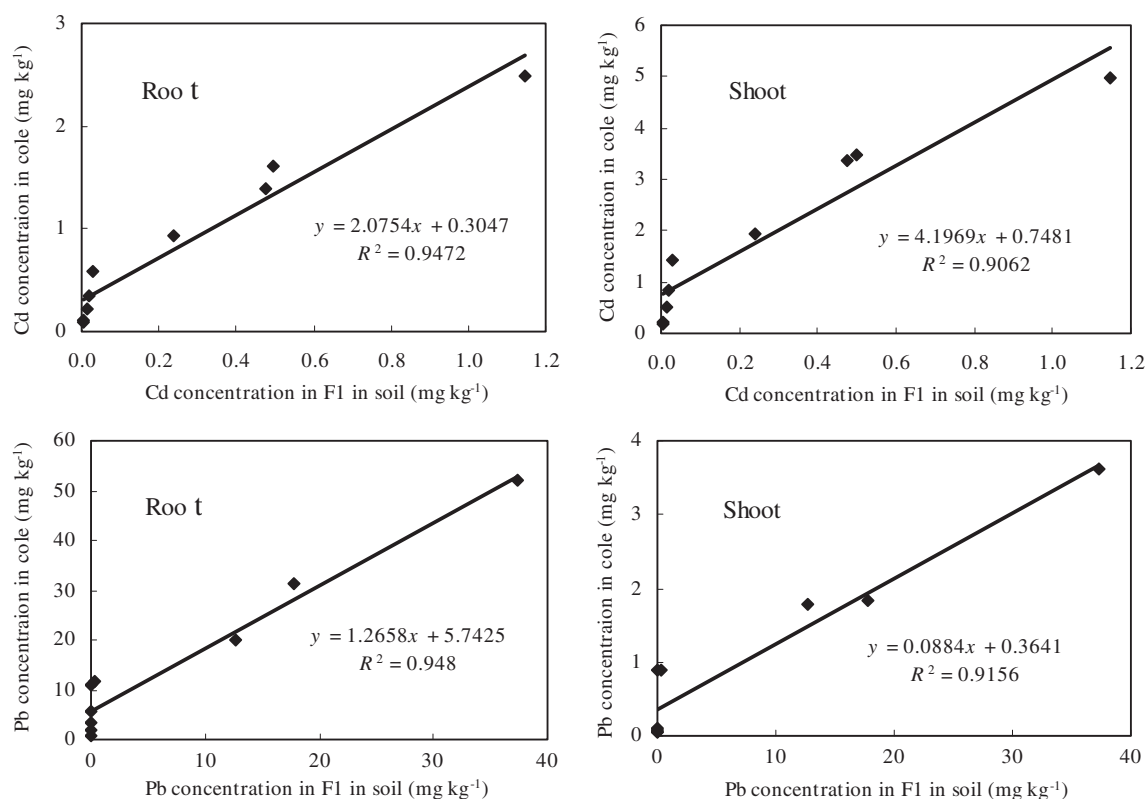


Figure 4. Stepwise regression analysis between the concentrations of Cd and Pb fractionation in F1 in soil and those in cole.

Table 3. Correlation coefficients (R) between the F1 fraction distribution coefficients (FDC) of Cd and Pb in the soil and concentrations of Cd and Pb in cole roots and shoots ($n = 9$).

Chemical fractions	R (Cd)		R (Pb)	
	Root	Shoot	Root	Shoot
F1	0.934**	0.948**	0.945**	0.938**
F2	-0.203	-0.134	0.750*	0.737*
F3	0.317	0.239	-0.836**	-0.798*
F4	-0.651*	-0.697*	-0.796**	-0.804**
F5	-0.788**	-0.825**	-0.550	-0.548

*Significant at level $p < 0.05$.

**Significant at level $p < 0.01$.

Xu et al. [58] found that Cd–Pb compound pollution had a synergistic effect on Cd, and Pb could promote Cd uptake in cole on red soil (pH 5.05). However, Cd–Pb compound pollution had an antagonistic effect on Pb, and Cd could restrain Pb uptake in cole. Li et al. [59] reported that the effect of Pb on cole assimilating Cd and the effect of Cd on cole assimilating Pb was not discovered under Cd–Pb compound pollution in Meadow cinnamon soil (pH 7.40). Lv et al. [57] observed that Cd–Pb had a synergistic effect on the Cd uptake of cole in rice soil (pH 6.48), but antagonistic effect on its Pb uptake. The present study (pH 7.80) is inconsistent with previous reports probably due to the different soil type.

Relationship between the accumulation in cole and chemical fractions of Cd and Pb in the soil

Significantly positive correlation ($p < 0.01$) was found between the FDCs of Cd and Pb in F1 in the soil and Cd

and Pb concentrations in cole roots and shoots, respectively (Table 3), the corresponding correlation coefficients of Cd were 0.934 for roots and 0.948 for shoots, respectively; and those of Pb were 0.945 for roots and 0.938 for shoots, respectively.

Liu et al. [37] reported that the carbonate- and Fe–Mn oxide-bound forms of Cd and Pb were the most available for cole uptake from meadow cinnamon soil (pH 8.24, stepwise regression analysis between the concentrations of Cd and Pb fractionation in soil and those in cole). Zhou et al. [39] found that exchangeable form and carbonate form made the most contributions to the content of Cd and Pb in roots of cole, while carbonate form made the most contributions to the content of Cd and Pb in stems and leaves from oasis soil (pH 8.47, stepwise regression analysis between the concentrations of Cd and Pb fractionation in soil and those in cole). These conclusions were not in agreement with present study (pH 7.80, stepwise regression analysis between the FDC of Cd and Pb in

soil and those in cole) probably because of different soil properties and regression analysis method. The present study showed that both exchangeable Cd and Pb (F1) were the most available fraction for cole, which indicated that both Cd and Pb in F1 made the greatest contributions on the accumulation of Cd and Pb in the roots and shoots of cole (Table 3 and Figure 4).

Yang et al. [14,15] reported that there was significantly negative correlation between the percentage of Cd in F5 in the soil and the accumulation of Cd in the roots and shoots of both cole and celery. In present study, significantly negative correlation was also observed between the FDCs of Cd in F5 and Pb in both F3 and F4 in the soil and Cd and Pb concentrations in cole roots and shoots, respectively (Table 3), which indicated that Cd in F5 and Pb in both F3 and F4 were unavailable fraction for cole.

Conclusions

Cadmium (Cd) in the unpolluted soil was mainly bound to carbonate fraction (F2) and Fe–Mn oxide fraction (F3), and lead (Pb) was mainly bound to carbonate fraction (F2) and residual fraction (F5). However, the fractional distribution of Cd and Pb changed significantly with increasing Cd and Pb concentrations in soil, where the concentrations of Cd in F1 (exchangeable fraction), F2 and F3, and Pb in F1, F2, F3 and F4 increased significantly.

Relatively lower concentrations of Cd and Pb could facilitate the growth of cole, but their growth was inhibited at higher concentrations. There was antagonistic effect between Cd and Pb in Cd–Pb compound pollution soil. Both Cd and Pb in F1 made the greatest contribution in the accumulation of Cd and Pb in cole. Both bioaccumulation factor and TF of Cd in cole were higher than Pb, and Cd had higher accumulation in the edible part of cole.

Therefore, Cd in cole grown in the Cd–Pb polluted soil has a higher potential of risk to human health, but Pb has a lower risk according to individual consumption figures for cole which is approximately 0.30 kg average per person per day.

Disclosure statement

No potential conflict of interest was reported by the authors.

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