A model for evaluation of the phytoavailability of trace elements to vegetables under the field conditions

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Abstract

Currently, several single extraction methods are used for the evaluation of the phytoavailability of metals using pot experiments. A systematic comparison, however, is lacking. It is especially true for the field studies. This study was to investigate the phytoavailability of trace elements to vegetables grown on metal-contaminated soils under the field conditions. All soils collected were typical calcareous soils in northern China. Four frequently used methods using CaCl_2 , diethylenetriaminepentaacetic acid (DTPA), CH_3COOH , and water as extractants were compared for phyto-availability. The concentrations of metals extracted by these four extraction methods ranged from 3.42 to 815, 1.51–6965, 0.732–24473, 0.688–7863, 0.246–685, 1.99–5337 0.203–4649 ng/g for Cr, Ni, Zn, Cu, Cd, Pb and REEs, respectively. Simple correlation analysis indicated that a significant correlation (Cr: $r = 0.5411^{**}$; Zn: $r = 0.6352^{**}$; Cd: $r = 0.6979^{**}$; Pb: $r = 0.5537^{**}$ and REEs: $r = 0.5185^{**}$ – 0.6684^{**}) was observed between the CaCl_2 -extractable metals in soil solution and that in Chinese cabbage. In addition, soil pH, organic matter (OM), and cation exchange capacity (CEC) also affect the phytoavailability. An empirical model was developed to express the combined effect of soil properties on the phytoavailability. The stepwise multiple regression analysis demonstrated that the phytoavailability of trace elements strongly correlated with the extractable fraction by CaCl_2 , total metal concentration in soils, and soil pH, OM, CEC. This model can describe approximately 75–95% of the variability of metal uptake and the r^2 values ranged from 0.741^{**} to 0.954^{**}, which were much better than the single correlation analysis. For celery and cole, a strong correlation was obtained for Cr, Ni, Zn, Cu, Cd, La, Ce, Pr and Nd. For spinach and Chinese cabbage, however, a positive correlation was only observed for 1 and 3 metals, respectively. Generally, the developed empirical model can integrate the combined effects of soil properties, extractable metal fractions in soil solutions and plant species on the phytoavailability of metals to vegetables in the field conditions.

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1. Introduction

Consumption of vegetables is one of the most important pathways by which heavy metals enter the

food chain. Both the farmland and urban environment often suffer from the metal contamination due to the irrigation with wastewater and traffic emission. Therefore, human exposure to contaminations of soils and vegetables is a matter of health concern. In soil–plant system, the risk assessments often include physico-chemical characteristics of soils (e.g. organic matter content, pH, and CEC). However, these risk assessments are often erroneous and unrealistic based on the availability of metals in freshly spiked soils or pot

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experiments or the crop plants. Soil is a heterogeneous system, which shows significant variability and may be influenced by external factors such as climate and human agricultural practices. A survey of literature shows there is no report on the phytoavailability of metals in soils to vegetables under the field conditions.

It is common conception nowadays that the total concentrations of metals in soils are not a good indicator of phytoavailability, or a good tool for potential risk assessment, due to the different and complex distribution patterns of metals among various chemical species or solid phases (Chen et al., 1996). The experimentally defined chemical procedures have been applied to identify plant-available forms of trace metals in soils. The most widely used methods for the evaluation of the availability of metals in soils are single extraction (Lindsay and Norvel, 1978; Leschber et al., 1985) and sequential extraction methods (Tessier et al., 1979; Ure et al., 1993). However, the sequential extraction methods are rather laborious and time consuming. Among single extraction methods, CaCl_2 and DTPA were the most widely used extractants (Novozamsky et al., 1993; Houba et al., 1996). DTPA (containing 0.01 M CaCl_2 , pH 7.3 and 0.1 M triethanolamine) is suitable for calcareous soils, as it is buffered at a pH 7.3 and therefore prevents CaCO_3 from dissolution and releases of occluded metals (Lindsay and Norvel, 1978). The CH_3COOH is the first step of a three-stage sequential extraction procedure recommended by European Community Bureau of Reference (BCR) (Ure et al., 1993). The extraction with water is to simulate the metal distribution equilibriums of metals in soil pore water.

It has long been recognized that the soluble, exchangeable and loosely adsorbed metals are quite labile, and hence more available for plants (Kabata-Pendias, 1993). Therefore, in order to assess the environmental risk and the phytoavailability of metals, efforts should be concentrated on the measurements of these available fractions. In this context, the phytoavailability of metals in soils to vegetables has been estimated by above-mentioned four single-extraction methods in order to give ideas on mechanisms responsible for metal uptake. Numerous literatures have reported that the soil characteristics can affect the phytoavailability of metals (Mcbride et al., 1981). The aim of the present study was to evaluate the combined effect of soil properties on the phytoavailability. Therefore, an empirical model was developed to correlate the metal phytoavailability with common soil properties and with metal concentrations in the extractable soil fractions obtained by the above-mentioned extraction methods. This allows the assessment of the potential abilities of the vegetables to mobilize or to accumulate metals from soils. The implication to human health can be evaluated by estimating the consumption of vegetables growing on the metal-contaminated soil.

2. Materials and methods

2.1. Soils

All sampling sites were concentrated in northern China. Surface soil samples (0–10 cm) were collected from the vegetable yard of 14 cities. These soils were calcareous soil and are affected by different anthropogenic sources of pollution: mine works, steel factory and highway emission. Among these sample sites, Yantai, Dalian and Beidaihe are tour cites; Beijing is the capital of China; Tianjing, Huludao, Yingkou, Zhengzhou, Jinan, Linyi and Xingxiang are all industrial cities. Fuyang and Hanzhong are small cities with small factories. The soil loosely adhered to roots were gently shaken off and the rhizosphere soil adhering to roots were separated by hands. Five to six grams of rhizosphere soils were sampled. One portion of the moist rhizosphere soils was stored in refrigerator for the metal fraction extraction and another portion was air-dried and sieved through a 2-mm nylon mesh for total metal analysis and water content measurement.

2.2. Plants

Four common vegetables, Chinese cabbage [*Brassica campestris* L. ssp. *pekinensis* (lour) Olsson], spinach (*Spinacia oleracea* L.), celery (*Apium graveolens*) and cole [*Brassica cumpestris* L. ssp. *chinensis* (L.) Makino, var. *communis* Tsenetlee] were collected from vegetable garden and three crops of each species were randomly selected. All selected plants were 6–8-week growth period and maturity. The crop quality was good for all vegetables. The vegetables were separated into roots and leaves (including stems). Roots and leaves of different vegetables were successively washed with tap water first to remove all visible fine soil particles and then with distilled water. The vegetables were oven-dried at 60 °C for 48 h before metal determination.

2.3. Characteristics of soils

Soil pH was measured using 1:2.5 (w:v) soil/de-ionized water ratio. Organic matter was determined by the Walkley-Black procedure (Nelson and Sommers, 1982). Cation exchange capacity (CEC) was determined by the method described by Rhoades (1982). These soil properties are listed in Table 1.

2.4. Single soil extraction

The operating schemes of all single-extraction methods employed in this study were consistent with the corresponding literatures (Lindsay and Norvel, 1978; Novozamsky et al., 1993; Ure et al., 1993; Houba et al.,

Table 1
Characteristics of soils

Soil no.	OM (%)	pH	CEC (meq/100 g)
1: Beijing	3.58	7.64	92.3
2: Beidaihe	0.899	7.09	109
3: Tianjing	4.27	7.25	51.6
4: Huludao	2.12	7.35	53.4
5: Yingkou	2.19	6.66	51.6
6: Dalian	4.36	6.91	62.9
7: Zhengzhou	1.09	6.99	76.8
8: Jinan	5.68	7.05	112
9: Linyi	1.68	6.55	56.3
10: Yantai	0.705	6.32	48.6
11: Xinxiang 1	1.28	6.65	124
12: Xinxiang 2	4.56	7.50	133
13: Fuyang	1.05	7.25	76.1
14: Hanzhong	1.56	6.89	30.2

1996). One gram of moist rhizosphere soil was used for metal fractionation.

2.5. Determination of trace elements

The dried soil samples were used for the determination of metals. A portion of 0.1000 g soil was digested with 3 ml HNO_3 /1 ml HClO_4 /1 ml HF (Zhang and Shan, 1997). For vegetables 0.3000 g of roots or leaves were digested with 1 ml HNO_3 /1 ml HClO_4 only. The concentrations of trace elements after sample digestion were determined by ICP-MS (Plasma Quad III, UK). A solution of ^{115}In at 20 ng/ml in 1% HNO_3 was used as an internal standard to compensate for matrix suppression and signal drifting during metal determination. The detailed operating condition of ICP-MS was reported previously (Li et al., 1998).

All reagents used were of analytical reagent grade or better. Statistical analysis was performed by use of SPSS software.

3. Results and discussion

3.1. Characteristics of soils

As shown in Table 1, soil pH values ranged from 6.32 to 7.64. For soil samples collected from Linyi, Yantai and Xinxiang (Table 1) the soil pH are slightly acidic. The Xinxiang soil 2 was irrigated with wastewater and its soil pH was slightly higher than pH of Xinxiang soil 1 with no wastewater irrigation. The organic matter contents varied from 0.7% to 5.6% among these soils, suggesting that the fertilizer levels in these soils were different. This discrepancy may influence the growth of vegetables and further influence the phytoavailability of metals. It was noticeable that Xinxiang soil 2 has higher

OM content than that of Xinxiang soil 1, which means that wastewater irrigation significantly increased the organic matter content in soils. CEC values of these soils were ranged from 48.6 to 112 mmol/kg. Xinxiang soil 1 and Xinxiang soil 2 have quite similar CEC values, indicating that the wastewater irrigation did not significantly change the cation exchange capacity of soils.

3.2. Soil contamination status of heavy metals

Total metal contents in soils (mg/kg, dry mass) are presented in Table 2. In addition, Table 3 lists the critical limits of soil metal concentrations of China and Denmark (Wang et al., 2001a,b; Lise et al., 2002) and the average values of USA, Japan and UK. The critical limits were defined as the values above which the toxicity was considered to occur. Compared the metal contents in Chinese soils with the critical limits and average content levels, it was quite clear that slight contamination of Cd, Pb and Cu was occurred in several locations in northern China.

Generally, the soil heavy metal contaminations in north China were fortunately not so severe although the contamination levels were more or less higher than that in USA, but quite similar to that in Japan and Britain. Based on the critical limits, all sampled soils can be divided into uncontaminated soils, slightly contaminated soils and medium contaminated soils. In the uncontaminated soils (Dalian, Yantai, Fuyang, Hanzhong), the concentrations of metals were below the soil quality criteria. In Beijing, Zhengzhou, Jinan, Xinxiang 2 soils, the concentrations of Cd and Pb were close to the advisory intervals, whereas the concentrations of the remaining metals were below the soil quality criteria. In the contaminated soil (Beidaihe, Tianjing, Huludao, Linyi), the mean concentrations of heavy metals were above the criteria limit of Chinese EPA. For example, Linyi soil has much higher copper content (239 mg/kg, dry mass), nickel content (73.9 mg/kg, dry mass) than other soils, which was above the critical range. The reason for the higher copper, nickel levels was ascribed to a large copper–nickel mine located there and it may contribute to this pollution problem. Up to 4 mg/kg of soil Cd, 200 mg/kg of soil Pb were detected in Huludao, a small city of Liaoning Province of China, where several large smelting factories and rock oil factories were located there. In Tianjing city, especially in Beijing–Tianjin–Tangshan area, wastewater irrigation caused soil contamination problem. Because the soils sampled are the surface soil (0–10 cm), soil Pb content was enhanced by atmospheric deposition in the vicinity of heavy industry, or the traffic emission. This is the reason for the large-scale Pb pollution in the investigated soils.

Unavoidably, some heavy metals deposited in the sludge were transferred to soils simultaneously. Xinxiang soil 2 has higher metal concentration (Cr, Cd and

Table 2
Total concentrations of trace metals in 14 soils (mg/kg, dry mass)

Soil site	Elements									
	Cr	Ni	Zn	Cu	Cd	Pb	La	Ce	Pr	Nd
Beijing	40.8 ± 1.3	28.9 ± 0.25	107 ± 4.5	33.3 ± 1.5	1.07 ± 0.056	98.6 ± 3.2	39.5 ± 1.9	54 ± 2.3	8.58 ± 0.096	25.3 ± 1.1
Beidaihe	48.6 ± 0.58	40.5 ± 0.61	205 ± 6.9	130 ± 6.9	1.62 ± 0.062	107 ± 4.1	2.5	107 ± 8.2	15.2 ± 0.62	45.4 ± 1.6
Tianjing	80.6 ± 2.5	40.3 ± 0.39	176 ± 5.3	91 ± 3.8	3.28 ± 0.21	155 ± 3.1	43.7 ± 2.5	64.8 ± 5.1	9.12 ± 0.65	27.9 ± 1.3
Huludao	80.5 ± 2.1	46.4 ± 1.65	117 ± 6.7	61.7 ± 3.3	4.08 ± 0.65	210 ± 5.9	49.6 ± 1.9	87.3 ± 6.2	10.4 ± 0.42	33.8 ± 1.5
Yingkou	69.4 ± 1.6	29 ± 0.27	61.3 ± 3.5	36.5 ± 1.4	3.07 ± 0.53	91.7 ± 1.2	38.2 ± 1.6	60.3 ± 3.2	9.16 ± 0.33	31.4 ± 1.3
Dalian	33.6 ± 0.33	24.6 ± 0.13	104 ± 3.9	31.1 ± 1.6	1.08 ± 0.064	29.9 ± 0.11	24.4 ± 0.69	40.8 ± 1.5	5.11 ± 0.25	20.9 ± 1.05
Zhengzhou	39.1 ± 0.69	18.9 ± 0.15	45.3 ± 2.7	20.6 ± 1.1	1.03 ± 0.055	78.2 ± 1.6	16.2 ± 0.25	29.4 ± 0.99	4.3 ± 0.11	13.2 ± 0.62
Jinan	64.2 ± 0.98	30.8 ± 0.39	59 ± 1.9	29 ± 1.6	1.17 ± 0.087	115 ± 1.3	30.4 ± 1.3	53.2 ± 1.6	8.06 ± 0.19	22.6 ± 1.3
Yantai	47.4 ± 0.85	20.3 ± 0.11	37.3 ± 1.5	24.1 ± 1.3	0.592 ± 0.032	20.1 ± 0.16	27.7 ± 0.85	49.4 ± 1.4	6.49 ± 0.17	19.4 ± 0.53
Linyi	160 ± 4.6	73.9 ± 1.5	35 ± 1.3	234 ± 10.6	1.52 ± 0.065	100 ± 2.3	34.9 ± 1.0	58.6 ± 1.9	9.11 ± 0.29	24.9 ± 0.96
Xinxiang 1	9.05 ± 0.21	6.39 ± 0.23	7.94 ± 0.98	10.9 ± 0.96	0.52 ± 0.033	20.2 ± 0.13	2.96 ± 0.015	4.29 ± 0.068	0.512 ± 0.009	1.66 ± 0.033
Xinxiang 2	86.1 ± 3.1	10.8 ± 0.24	13.5 ± 0.68	49 ± 2.6	3.56 ± 0.15	55.2 ± 0.26	3.41 ± 0.013	5.63 ± 0.011	1.09 ± 0.065	4.26 ± 0.098
Fuyang	20.3 ± 0.55	11.5 ± 0.18	12.4 ± 0.77	6.71 ± 0.32	0.0538 ± 0.002	68.7 ± 3.2	10.3 ± 0.23	16.6 ± 0.006	2.01 ± 0.024	6.15 ± 0.067
Hanzhong	39.5 ± 0.68	8.43 ± 0.14	31.1 ± 2.1	7.89 ± 0.55	0.054 ± 0.002	61.3 ± 2.6	1.81 ± 0.006	3.15 ± 0.009	0.391 ± 0.003	1.54 ± 0.025
Mena	58.4	27.9	72.2	54.7	1.65	86.4	28.9	45.3	6.39	19.8

Pb) than Xinxiang soil 1. This was an evidence for the possibility of sewage contamination. Long-term application of metal-containing chemicals, such as Cd-containing phosphate fertilizers, Pb-, and Zn-containing pesticides, in agriculture could also result in soil contamination (McGrath, 2000). Wang et al. (2001a) have investigated the current status of soil contamination with heavy metals and sources of pollutants. Their investigation demonstrated that metal-containing agrochemical application in agriculture, e.g. Cd-abundant phosphates and the untreated electric planting wastewater irrigation usually lead to the elevated Cd content in soils.

3.3. BCF values of vegetables

BCF values were always used to describe the accumulation of chemicals in organisms, especially, those live in contaminated environments. BCFs were used to relate pollutant residues in organisms to the pollutant concentration in the environment. The BCF value can be calculated based on the ratio of metal concentrations in plants to soil. In our experiment, we considered heavy metals in vegetable leaves as the absorbed metal amounts or heavy metal residues in plants (Krishnamurti and Naidu, 2002). BCF values of heavy metal for four vegetables in uncontaminated soils, slightly contaminated soils and medium contaminated soils are shown in Fig. 1. Our experimental results indicated that the BCF values of all four vegetables decreased with increasing metal contamination in soil, especially for the more mobile metals (Cd and Zn), for which the highest BCF values were found. This fact was observed by Lise et al. (2002). The high BCF values may exert potential risk to human health. There were two possible reasons for the interpretation why BCF values decreased with increasing soil contamination. One possible reason was that the self-adjusting of plants plays an important role on sequestering the metals in their roots. Only small amounts of metals are translocated to the up-ground parts of plants. In slightly contaminated soils, plants grow well and the metal concentration in plant leaves is at a similar level to or higher than that grown on clean soils. However, the corresponding metal contents of soils are much higher than the clean soil, and hence the BCF values of plants grown on slightly contaminated soils were decreased. Another possible reason is that plants grow badly on the contaminated soils. It is especially true on the heavily contaminated soil, plants become blasted and gradually die. In this case, because of the bad living condition, the metal uptake ability by plants was weakened, and the metal content in plant leaves was decreased. On the contrary, the corresponding metal content of soils was quite high, so the BCF values of plants in heavily contaminated soils were significantly decreased. All vegetables investigated in this

Table 3
The critical limit and average level of metals in soils (mg/kg, dry mass)

Elements	Critical limit of metals in soils			Average level of metals in soils		
	China		Denmark Background soils	USA	Japan	Britain
	Cultivated soils	Background soils				
Cr	200	35	50	54	41.3	84
Ni	50	40	10	19	28.5	33.7
Zn	250	100	30	25	37	25.8
Cu	100	35	100	60	63.8	59.8
Cd	0.6	0.2	0.3	—	0.413	0.62
Pb	300	35	40	19	20.4	29.2

Fig. 1. BCF values for heavy metals in experimental soils.

paper showed good qualities. And if plants with good qualities were selected from contaminated soils, the metal content of plants would be higher than that selected from clean soils. Good qualities of plants concealed the fact of contamination and then induced the harmful effect to human health.

3.4. Single extraction methods for prediction of the phytoavailability of heavy elements in soils to vegetables

Currently, the phytoavailability of metals in soils to plants is generally determined by correlating the concentrations of metals in plants with that in various soil fractions determined by single and/or sequential extraction procedures. The phytoavailability varies with plant species and properties of given soils. In this paper,

we use single regression and multiple regression analyses to compare the suitability of various extraction methods for phytoavailability of heavy metals under the field conditions. The positive correlation suggests that the extraction procedure is suitable for the evaluation of metal accumulation in plants. However, the negative correlation means that this extraction method cannot illustrate the accumulation of metals to vegetables.

Table 4 lists the range of metal concentrations in the different extractable fractions and Tables 5 and 6 display the correlation coefficients obtained by single regression analysis. The metal concentrations with four extractants were ranged from 3.42 to 815, 1.51–6965, 0.732–24473, 0.688–7863, 0.246–685, 1.99–5337 0.203–4649 ng/g for Cr, Ni, Zn, Cu, Cd, Pb and REEs, respectively. The CH_3COOH - and DTPA-extractable metals are higher than

Table 4

The extractable metal contents of different extractants (ng/g, dry mass)

	CaCl ₂	DTPA	CH ₃ COOH	H ₂ O
Cr	20.4–65.5	37.2–244	154–815	3.42–91.5
Ni	51.1–406	8.45–175	19.9–6965	1.51–197
Zn	5.82–2595	39.7–16 171	59.8–24 473	0.732–335
Cu	32.2–4401	253–7863	152–2817	0.688–299
Cd	1.69–182	7.46–436	6.25–685	0.246–52.6
Pb	40.5–5322	601–5337	112–3056	1.99–332
La	6.62–3017	47.2–1805	115–605	0.373–59.4
Ce	10.4–3890	79.2–2516	120–87.6	1.27–193
Pr	1.80–650	11.9–1201	16.2–132	0.346–14.5
Nd	5.43–2092	36.9–4649	76–1469	0.203–41.5

Table 5

Correlation coefficients between the extracted metal concentrations in 14 soils and metal concentrations in roots of four vegetables

	Chinese cabbage		Spinach		Celery		Cole	
	CaCl ₂	DTPA	CaCl ₂	DTPA	CaCl ₂	DTPA	CaCl ₂	DTPA
Cr	0.5411**	0.7105**	0.4119	0.7238**	–0.2671	0.4925*	0.2187	0.5083*
Ni	0.01226	0.09823	0.0793	–0.4396*	–0.1368	0.00304	–0.04146	0.1005
Zn	0.6352**	0.3623	0.3328	0.2566	0.5859**	0.3687	0.8511**	0.3469
Cu	0.1415	–0.06819	–0.00921	–0.1434	–0.1493	0.1557	0.2251	0.01306
Cd	0.6979**	0.5206**	0.4716*	0.4625*	0.7215**	0.6862**	0.4268*	0.5518**
Pb	0.5537**	0.6914**	0.5492**	0.6507**	0.5519**	0.09117	0.5765**	0.5549**
La	0.5185**	0.4953**	0.6217**	0.4845**	–0.1477	–0.1727	0.8837**	0.5838**
Ce	0.6684**	0.5202**	0.5649**	0.4394*	–0.1288	0.2525	0.7116**	0.5518**
Pr	0.5502**	0.2708	0.4799**	0.5095**	–0.1493	–0.05887	0.9542**	0.5579**
Nd	0.5233**	0.5594**	0.5079**	0.5012**	–0.1139	–0.04392	0.6102**	0.6796**

* and ** significance at 10% and 5% level, respectively.

Table 6

Correlation coefficients between the extracted metal concentrations in 14 soils and metal concentrations in the shoots of four vegetables

	Chinese cabbage		Spinach		Celery		Cole	
	CaCl ₂	DTPA	CaCl ₂	DTPA	CaCl ₂	DTPA	CaCl ₂	DTPA
Cr	0.3852	–0.5768*	0.4104*	–0.7417**	0.4993**	–0.6529**	0.2601	–0.5465
Ni	0.2945	0.05408	0.2587	–0.5653**	0.3786	–0.4406	0.4527	–0.3258
Zn	0.202	–0.3939	0.3032	0.01291	0.5806**	–0.1644	0.3936	–0.04584
Cu	0.2355	–0.2864	0.8233**	–0.0444	0.8995**	–0.07706	0.106	–0.3597
Cd	0.2236	0.04744	–0.2217	0.1244	–0.34715	–0.05717	–0.1537	–0.2463
Pb	0.8045**	0.7204**	0.4489*	0.4813*	0.6397**	–0.3883	0.6449**	0.6585*
La	0.0542	0.2434	0.7473**	0.4944**	0.5999**	0.3472	0.4665*	0.8046**
Ce	0.2256	0.1032	0.7177**	0.5659**	0.2699	–0.05079	0.4988**	0.7921**
Pr	0.2434	0.1258	0.6343**	0.4422*	0.6715**	0.5726**	0.4529*	0.7748**
Nd	0.1635	0.1528	0.6492**	0.4779*	0.4051	0.3373	0.4432	0.7373**

* and ** significance at 10% and 5% level, respectively.

other that extracted by other extractants. Water extractable metals were the lowest one. As can be seen from these tables, the correlation coefficients of roots were prevalently better than that of shoots, suggesting that vegetable roots were a good indicator of metal phytoavailability. In calcareous soils high soil pH was likely to promote the release of more metals from soils. The released metals were easily accumulated in plant

roots (Chaignon et al., 2003). This may also be the possible reason to interpret why roots have good correlation coefficients. From these correlations, we found that the root metal concentrations increased with increasing metal concentrations in the extractable fractions of soils. Besides Cr, Zn, Cd and Pb, the concentrations of REEs always revealed better correlations with plant roots (for spinach, good correlations were

also found in its shoots for REEs). This discrepancy existed among heavy metals and rare earth elements may be caused by the different elemental speciation in soils. A widely accepted opinion is that the metal uptake by roots occurs from soil pore water. For some metals, such as Zn and Cd, they are primarily as soluble or exchangeable, readily bioavailable forms (Lasat, 2002). These bioavailable forms can be easily taken by plant roots, which explained the reason for good correlation coefficients. However, it should be pointed out that correlation between concentrations in plant roots and extracted fractions was poor for Cu.

CaCl_2 is the primary component of soil background electrolytes. The exchangeable cations may be displaced by the basic cations commonly present in extraction solutions (Ca^{2+}). Heavy metals and REEs, which are originally absorbed by soils will be competed by calcium ions and be replaced from the binding sites. Compared to other methods employed in this paper, 0.01 M CaCl_2 seems to be the best one based on the good correlations, which suggests that the plants are able to take up the great mass of the metals extracted by CaCl_2 . DTPA, and CH_3COOH are all chelating reagents. DTPA extractable metals were correlated with metal concentrations in plant roots well. The reason why DTPA shows a better correlation may lie in the fact that the DTPA extractant contains a high concentration of CaCl_2 , of which Ca^{2+} may exchange rapidly with bivalent cations, especially Cd^{2+} and Zn^{2+} from soils. DTPA contains triethanolamine (TEA), which is protonated at pH 7.3 and could exchange H^+ with cations from the exchange sites as suggested by Lindsay and Norvel (1978).

Using organic acids to extract bioavailable metals from soils has been accepted because organic acids can dissolve the particulate-bound metals into soil solution and are exudates of plant roots (Cieslinske et al., 1998). From our investigation, CH_3COOH showed good relations only for Cd. Although acetic acid comprise the largest component of total organic acids in rhizosphere soil of plants (Baziramakenga et al., 1995), formic acid, citric acid and malic acids are frequently found to be the other major components of total organic acids and have relatively abundant concentrations (Jones et al., 1996). Of course, the ratio of these organic acids varies from soil to soil and from plant to plant as well. Therefore, the soil fraction extracted only by acetic acid provides no insight into the real amount of metals transferred from soil to plant.

It should be pointed out that water-extractable metals were not at all correlated with the concentration of metals in vegetables except for Chinese cabbage. The correlation coefficients between the extracted metal concentrations by CH_3COOH and water are not included in Tables 4 and 5.

Lead is strongly bound with soil particles, which renders a significant soil Pb fraction insoluble, display-

ing a low phytoavailability. However, Pb contents in plant shoots indicated remarkable positive correlations with that of CaCl_2 -extractable Pb (i.e., $r = 0.8045^{**}$ for Chinese cabbage). Even water-extractable Pb shows a good correlation with Pb contents in plant shoots ($r = 0.6153^{**}$ for Chinese cabbage) and roots ($r = 0.7030^{**}$ for Chinese cabbage). These good correlations demonstrated that the exchangeable Pb, water soluble Pb were the bioavailable to vegetables. One source of Pb contamination in soil was probably from air pollution. Although the use of gasoline containing Pb has been forbidden for several years, the sedimentation rate of Pb was reported to be very slow from the surface soil to deep-seated soil (Lasat, 2002). Studies have showed that the availability of metals is considerably reduced by aging, due to the formation of strong bonds to soil particles and/or incorporation into resistant secondary minerals of low phytoavailability (e.g., iron oxides). As for the young flue-dust contaminated soils, Pb existed in the surface soil was loosely associated with soil particles and was easily dissolved by soil pore water or exchanged by Ca^{2+} . This is the reason why Pb contents in plant shoots shows positive relations with that of CaCl_2 - and water-extractable Pb in soil solution. As for the different plants, the celery behaved the worst correlation coefficients for REEs, suggesting the complexity of plant uptake of trace elements and the diversity of the microcosmic process of plant rhizosphere.

3.5. Relationship between soil properties and extractable metals of CaCl_2 and DTPA

Table 7 demonstrates the relationships between the metal contents in extractable fractions and soil properties (OM, pH, CEC). As can be seen from this table that CaCl_2 and DTPA methods showed different correlations with soil properties. This may due to the different extraction mechanisms. Ca^{2+} can exchange and then replace most of divalent metal ions from their binding sites of soil particles. DTPA, a strong chelator for metals, can even extract metals from other metal-organic complexes (Hammer and Keller, 2002). This is the reason why the concentrations of many heavy metals in their DTPA extractable fractions can exhibit positive correlations with the soil organic matter contents, whereas CaCl_2 cannot.

Except for Ni and Cd, extractable metals exerted a positive linear correlation with soil pH when CaCl_2 was used as extractant. This result was supported by the viewpoints of Chaignon et al. (2003). Chaignon et al. (2003) suggested that the higher ambient pH of calcareous soils was likely to promote the release of more metals from soils, which were easily taken by plant root cells. However, for DTPA being buffered at pH 7.3, only copper exhibited positive pH-dependency.

Table 7

Single linear correlation coefficients between extractable metal concentrations and soil properties

	OM		pH		CEC	
	CaCl ₂	DTPA	CaCl ₂	DTPA	CaCl ₂	DTPA
Cr	0.238	0.403*	0.493**	−0.332	−0.677**	0.663**
Ni	0.279	0.504**	0.237	0.055	−0.463**	0.554**
Zn	0.234	0.442**	0.410*	0.364	−0.176	0.305
Cu	−0.167	0.503**	0.558*	0.580**	−0.619**	0.247
Cd	0.295	0.313	−0.262	0.115	0.501**	0.309
Pb	−0.125	0.162	0.550**	0.668**	−0.6591**	−0.0994
La	−0.184	−0.431**	0.571**	0.134	−0.651**	−0.741**
Ce	−0.161	−0.496**	0.578**	−0.000747	−0.663**	−0.423*
Pr	−0.195	−0.268	0.493**	0.199	−0.691**	−0.599**
Nd	−0.188	−0.201	0.480**	0.242	−0.699**	−0.597**

* and ** significance at 10% and 5% level, respectively.

The influence of CEC on the extraction using different extractants was discussed. The REEs concentrations in the extractable fractions of both CaCl₂ and DTPA were negatively correlated with CEC, demonstrating that REEs were more easily sequestered than other metals under higher CEC conditions. Stewart et al. (2003) have testified that the higher soil CEC generally has higher content of clay and organic matters, and hence show strong ability on the sequestration of metals. Because of the higher ion charge (trivalent of La and quadrivalent Ce, etc.) of REEs, the interactions occur between REEs and binding sites, thus retarding the release of REEs from the soil particles. Additionally, with the increase of CEC, Cr and Ni concentrations in the extractable fractions of DTPA increased too. Since the mechanism of Cr and Ni retardation on clay minerals (clay content of soils was the first most important determinant of the CEC value of soils) was primarily weak electrostatic-bond interaction, these bonds were easily broken under the extraction of a strong chelator of DTPA, allowing Cr and Ni desorbed from the soil and released into solution (Stewart et al., 2003).

3.6. Relationship between soil properties and the phyto-availability of metals to vegetables

The correlations between the metal concentrations in plant roots and soil properties are listed in Table 8. As for the effect of OM, only the phytoavailability of Cr and Cu expressed positive correlations with the organic matter contents of soils. Some literatures held the opinions that the metals combined with organic matters were difficult to be taken by plants. However, the opposite view was that the organic-binding metals can be easily decomposed by anaerobic metal-reducing bacteria and then be absorbed by plants. Soil Cu and Cr uptake by plants is an interesting area, and literatures have illustrated that Cu always combined with organic ligands of soils. The Cu–fulvic acid, Cu–humic acid complexes in soil solution seemed to be the forms easily taken by plants (Krishnamurti and Naidu, 2002). Stewart et al. (2003) also suggested that the concentration of Cr was higher in the organic-bound fractions than in the soluble and exchangeable fractions. Hansel et al. (2003) have investigated the microbial decomposition of Cr–

Table 8

Single linear correlation coefficients between metal concentrations of the roots of vegetables and soil properties

	OM				pH				CEC			
	Chinese cabbage	Spinach	Celery	Cole	Chinese cabbage	Spinach	Celery	Cole	Chinese cabbage	Spinach	Celery	Cole
Cr	0.447*	0.116	0.430*	0.586**	−0.168	−0.361*	0.179	−0.193	0.538**	0.443**	0.560**	−0.0229
Ni	0.0435	−0.299	0.0868	0.253	−0.387*	−0.261	0.175	−0.202	−0.217	−0.264	0.576**	−0.293
Zn	0.218	0.216	0.353	0.384	0.251	−0.322	0.189	0.195	0.0818	0.0956	0.339	−0.303
Cu	0.203	0.355*	0.623**	0.421*	−0.00074	0.187	−0.477*	0.35	−0.128	0.126	−0.490**	−0.512**
Cd	0.309	0.153	−0.0393	0.343	−0.422*	−0.23	0.272	−0.386*	0.118	0.139	−0.0847	−0.0931
Pb	−0.0722	−0.191	0.356	0.181	0.471*	0.505**	0.547**	0.415*	−0.614**	−0.406*	−0.614**	−0.527**
La	−0.0282	−0.122	−0.0598	−0.173	0.29	0.325	0.307	0.516**	−0.466*	−0.384*	−0.363	−0.631**
Ce	0.00276	−0.11	−0.0475	−0.00914	0.214	0.358	0.368	−0.0653	−0.475*	−0.365	−0.384*	−0.114
Pr	0.0761	−0.0984	−0.0881	−0.223	0.125	0.341	0.285	0.527**	−0.395*	−0.368*	−0.361*	−0.672**
Nd	0.0631	−0.0986	−0.173	−0.271	0.162	0.412*	0.223	0.523**	−0.447*	−0.364	−0.395*	−0.606**

* and ** significance at 10% and 5% level, respectively.

natural organic matter fractions. All these results supported the conclusion that higher soil OM enhanced the phytoavailability of Cr and Cu.

Considering the effect of soil pH on the phytoavailability of metals to vegetables, we found that only Pb uptake showed a positive pH-dependency. This positive correlation suggested that high soil pH could increase the availability of these metals to plants. Generally, with decreasing pH, pronounced increase in release rate of Pb was observed. The lower soil pH, the higher Pb^{2+} concentrations can be found in soil solution (Badawy et al., 2002; Sukreeyapongse et al., 2002). However, among these calcareous soils Pb in soils was probably from air pollution and the Pb^{2+} was loosely bond with soil particles. In that case, Pb^{2+} seems to be easily bound to root cell walls. Therefore, it was possible that a large proportion of Pb in plant roots were adsorbed by root cell walls due to the high ambient pH (Chaignon et al., 2003). Therefore, this reversed the positive dependence of soil pH on Pb uptake by plants, which was observed in this paper. As observed by other authors that Ni, Cd, Cu and Cr showed negative correlations between their uptake by plants and soil pH (Krishnamurti and Naidu, 2002; Stewart et al., 2003).

The uptake of Pb and REEs by different vegetables seems to be increased with the decrease of the cation exchange capacity of soils, which is evidenced by the negative correlation coefficients. This result was consistent with the results obtained for the relationship between metals in soil extractable fractions and soil CEC. It seems that metals in clay materials with higher CEC are not available to plants.

From these results, we concluded that the soil properties could remarkably influence the phytoavailability of trace elements. However, soil properties display more complicated effects on the phytoavailabilities of metals to plants. So it was very important to investigate the combined effects of these factors on the phytoavailability of metals to plants, especially under the real-field conditions.

3.7. Multiple regression analysis model for evaluation of phytoavailability

Principally, the single extraction and sequential extraction methods were based on the assumption that there was a relationship between the extractable fraction of metals and the phytoavailability of metals to plants, and a good correlation reflected that fraction of metals in soils was available to plants. However, it was not always true that a statistically valid correlation of soil-to-plant system could provide insight into the mechanisms of phytoavailability. Because the chemical, biological and physical mechanisms governed the translocation of metals from soils; therefore, high variability of phytoavailability was always observed in the literature. Con-

sidering this situation, we integrated soil pH, OM, CEC, total metal concentrations of soils and extractable metal concentrations in soil solutions together to simulate the combined effects of rhizosphere microenvironment, and an empirical model was derived to express the relationships between metal phytoavailability and properties of rhizosphere.

$$\log[M_{\text{root}}] = a + b \log[M_{\text{soil}}] + c\text{OM} + d\text{pH} + e\text{CEC} + f \log[M_{\text{extra}}]$$

where $[M_{\text{root}}]$ and $[M_{\text{soil}}]$ were the total metal concentrations in plant roots and in soils, respectively. $[M_{\text{extra}}]$ was the metal concentration in the extractable soil fractions. a – f were coefficients determined with statistical regression. According to this model, a step-wise multiple regression analysis was performed and the correlations were largely improved (Table 9). Besides this improvement, the model also passed the normality t -test, suggesting that the data was normally distributed around the regression line and that the variance presented in the dependent variable was constant. For the multiple linear regressions, the r^2 values can be used to explain the variation of the dependents. From this table we can see that the r^2 values were above 0.700 (extracted by CaCl_2), which means that more than 70% of variation in root uptake of trace elements can be described by soil pH, CEC, OM and metal concentrations. Among the extraction methods studied, CaCl_2 and DTPA gave better correlation coefficients. The r^2 values of these two methods were larger than that of other methods and the significance level was also satisfied. The multiple regression model was statistically rigorous at the 95% confidence level since P values for the independent variables were all <0.05 . Combined with the results obtained by the linear regression (Tables 5–7 and 9) one could conclude that under the real field conditions, CaCl_2 and DTPA methods were suitable for predicting the phytoavailability of trace elements in soils to vegetables. For the health risk assessments, the concentrations of trace elements in vegetables could be predicted by means of the equation.

The coefficients of each influence factor can be used to evaluate the influence ability of these factors. Table 10 lists the model parameters of different influence factors. For example, the recommended model suggested that Cr phytoavailability of celery was enhanced by higher soil metal contents, higher organic matter contents, higher CEC and lower soil pH (positive coefficients showed positive effect and vice versa). As the exchangeable metal fractions are assumed to be easily absorbed fractions to plants, the great contribution of total metal concentrations in soils indicated that some soil fractions of metals could also be absorbed indirectly through the decomposition of metal–organic matter complexes by microorganisms. According to the present model a

Table 9
Correlation coefficients obtained by multiple regression

		CaCl ₂	DTPA	CH ₃ COOH	H ₂ O
		<i>r</i> ² value			
Chinese cabbage	Cr	0.736**	0.807**	0.785**	0.748*
	Zn	0.689*	0.478	0.218	0.392
	Pb	0.717**	0.747**	0.798**	0.697
Spinach	Cr	0.885**	0.819**	0.819**	0.801**
Celery	Cr	0.849**	0.941**	0.956**	0.881**
	Ni	0.954**	0.861**	0.875**	0.867**
	Zn	0.834**	0.864**	0.864**	0.845**
	Cu	0.754**	0.717*	0.654	0.687
	Cd	0.898**	0.612*	0.541	0.439
	La	0.867**	0.773*	0.666	0.661
	Ce	0.757**	0.893**	0.777*	0.745*
	Pr	0.887**	0.765*	0.589	0.629
	Nd	0.874**	0.754*	0.612	0.647
Cole	Cr	0.769**	0.781*	0.772*	0.742*
	Zn	0.896**	0.838**	0.836**	0.664
	Cu	0.741**	0.791*	0.834**	0.748*
	Cd	0.749**	0.588	0.586	0.573
	Pb	0.825**	0.692*	0.496	0.421
	La	0.774**	0.498	0.497	0.519
	Pr	0.802**	0.768*	0.739*	0.746*
	Nd	0.806**	0.727*	0.659	0.629

* and ** significance at 10% and 5% level, respectively.

good fitting was achieved if total metal concentrations in soils were integrated. However, Cd uptake by celery was an exception even total soil metal concentrations and organic matter contents were not included in the model fitting, since the other three independent can describe approximately 90% of the variability of Cd uptake. Among the six parameters involved in this model, intercorrelated reaction between them are obvious, e.g., the metal concentration in the extractable fraction correlated with soil total metal concentration; concentration in the extractable fraction correlated with OM, pH and CEC etc. However, the coefficients obtained in this model can regulate these cross-effects and make the better model fitting. For example, as for celery, although there was correlation between the total Cr concentration of soils and the extractable Cr concentrations, both these two influences gave the positive effect on the phytoavailability of Cr. The total Cr concentration of soils was the leading influence factor on the phytoavailability of Cr to celery (the coefficient *b* was positive and greater than other parameters). However, this influence was not sufficient and need the extractable Cr concentration to complement (the coefficient *f* is also positive). As mentioned above, as for celery, only the extractable Cd significantly contributed to the phytoavailability of Cd (*f* = 3.12) and the total Cd metal concentration was not a main variable.

In Tables 8 and 9 there were different correlation coefficients for different plant species. As for celery, the total metal concentration influenced phytoavailability dominantly (great *b* values were observed, except for Cd). Nevertheless, the extractable metal concentration was the major contributor to the phytoavailability of metals to cole (except for Pb and Cd, great *f* values were observed).

It was interesting to note that for celery and cole, this model proved to be suitable for 9 metals (Cr, Ni, Zn, Cu, Cd, La, Ce, Pr and Nd). Nevertheless, as for spinach and Chinese cabbage, only 1 and 3 metals showed strongly correlations. Celery and cole, which had thriving rootlets and root hairs, exhibited excellent positive correlations if CaCl₂ and DTPA extraction methods were used. However, Chinese cabbage had straight roots and a few adnascent roots. Probably due to this fact only three elements displayed the positive relations. The spinach root is stout (no lateral root attached), which grows straight downward from the stem. This is the possible reason for only Cr showed positive relations. The more plant roots were thriving, the better correlations were obtained.

Based on the above study one could draw a conclusion that, on the one hand, soil properties affect the phytoavailability of metals in soils, such influences should be considered in the evaluation of phytoavailability. On the other hand, plant roots governed the

Table 10
Parameters for multiple regression analysis

		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
Celery	Cr	4.64	0.849	0.116	−0.205	0.00556	−1.38
	Ni	−1.12	1.11	0.0137	0.182	0.00647	0.514
	Zn	3.85	0.564	0.0604	−0.194	0.00289	0.145
	Cu	1.72	0.152	0.0661	0.246	0.00163	−0.00118
	Cd	−5.98	–	–	0.443	−0.114	3.12
	La	−0.282	0.688	0.00671	0.313	0.00233	−0.0514
	Ce	−0.693	0.739	0.00562	0.341	0.0308	−0.0172
	Pr	−1.67	0.695	−0.0294	0.516	0.00119	−0.174
Cole	Nd	−1.38	0.812	−0.0384	0.481	0.00111	−0.141
	Cr	3.98	0.191	0.0972	0.357	0.00269	0.711
	Zn	3.42	0.141	0.0109	−0.00252	-3.01×10^{-4}	0.283
	Cu	2.19	0.253	0.0632	−0.171	−0.00313	0.0755
	Cd	6.84	0.958	0.0993	−0.554	−0.00101	−0.375
	Pb	3.23	0.575	0.156	−0.545	0.00422	0.952
	La	5.32	−0.146	0.0722	−0.458	-7×10^{-4}	0.661
	Pr	4.26	−0.567	0.0328	−0.153	−0.0106	0.334
	Nd	−3.39	−0.281	−0.242	1.176	−0.0118	0.411

Note: *f* is the parameter of CaCl₂ extractable fraction.

metal availability, which was a forgotten area of study and was worthwhile research in the future. In a word, this model was more suitable for the plant, which had thriving rootlets and was applicable to predicting the phytoavailability of metals to the plants under the real field condition.

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