Simultaneous extraction of soil phytoavailable cadmium, copper, and lead by chelating resin membrane

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Abstract

Cadmium, copper, and lead were extracted from suspensions of contaminated soils using metal chelating exchange resin membranes. Nine soils with widely varying properties and Cd, Cu and Pb levels were tested. Soil suspensions made up with 4 g in 40 mL deionized water were equilibrated with 5 cm² Ca-saturated Chelex exchange resin membrane which was retained inside a polypropylene bag and shaken at 150 rpm for 24 hrs. Resin membrane extractable Cd, Cu and Pb of the soils were correlated with Cd, Cu, and Pb uptake by young wheat seedlings grown in these soils and compared with soil Cd, Cu, and Pb extracted by 0.1 M HCl, 0.01 M CaCl₂, and 0.005 M Diethylenetriamine pentaacetic acid (DTPA). The amounts of Cd, Cu and Pb extracted by the Ca-saturated Chelex membrane from all tested soils correlated well with those absorbed by young wheat seedlings. The Ca-saturated Chelex membrane extractable Cd, Cu and Pb of the soil had the strongest correlation with plant uptake Cd, Cu and Pb among the extraction methods we tested. It was demonstrated that the Ca-saturated Chelex membrane extraction is an appropriate method in simultaneously estimating Cd, Cu and Pb phytoavailability of soil and is applicable to a wide range of soils.

Introduction

Several soil diagnostic tests using chemical extractants have been proposed to estimate the phytoavailability of Cd, Cu, and Pb (Baker and Amacher, 1982; Risser and Baker, 1990). Phytoavailability, in this case, refers to availability of soil-borne metals to plant absorption and is customarily measured as amounts of metals absorbed by plants grown under optimal growing conditions. These methods were successful in estimating the phytoavailability of Cd, Cu and Pb in soils under limited conditions. But none of the methods has been able to predict consistently the phytoavailability of metal for soils of various physical and chemical properties.

Another approach to estimating metal phytoavailability of soil is to introduce a strong or infinite sink for soil metals. The infinite sink method is chemically less destructive to the soil and its reaction with the soil resembles the way plants extract elements from the soil. The ion exchange resins have been used as infinite

sinks in extracting available elements from soils (Amer et al., 1955; Sibbesen, 1977; Skogley et al., 1990). A chelating exchange resin is superior to an ion exchange resin in which trace metals must compete with much higher concentrations of metals such as Ca, Mg, and K. Jing and Logan (1991 and 1992) used chelating resin beads as infinite sinks in extracting plant available Cd from sewage sludges. Lee and Zheng (1993) reported a chelating resin membrane method for estimation of phytoavailability of Cd in the soil. Their results showed that Cd uptake by wheat seedlings has a stronger correlation with extractable Cd by the chelating resin membrane than with soil Cd extracted by four conventional chemical extraction methods for a variety of soils. In this study, the chelating resin membrane method to estimate phytoavailable soil metals was further evaluated with simultaneous extraction of Cd, Cu, and Pb of soils which had different physical and chemical properties and contained varying amounts of Cd, Cu, and Pb. Amounts extracted were correlated with Cd, Cu, and Pb absorption by wheat seedlings grown

on the same soils. The results were also compared with the amounts of Cd, Cu, and Pb extracted using other chemical extraction methods.

Materials and methods

Preparation of resin membrane

Sheets of Na-saturated chelating resin membrane (Chelex 12" × 12" membrane sheets, Bio-Rex ion exchange membrane sheets, Bio-Rad) were cut into 1 cm × 5 cm pieces. The Na-form of resin membrane was transformed into Ca-saturated form for use. The details of preparing the resin membrane, including transformation to Ca-form and regeneration of spent-membrane, were described by Lee and Zheng (1993).

Cadmium, Cu, and Pb adsorption by chelating resin membrane from metal solution mixture

A series of 50-mL centrifuge tubes each with one piece of the resin membrane (5 cm²) enclosed in a polypropylene (PP) mesh bag (60 mesh) were filled with 40 mL of solution containing 2 mg L⁻¹ Cd, 20 mg L⁻¹ Cu, and 24 mg L⁻¹ Pb. The tubes were then shaken at 150 rpm and 25°C for periods ranging from 2 to 30 hrs. At the end of shaking periods, the resin membranes along with the bags were recovered, rinsed thoroughly with deionized water, and air-dried. The membranes were then placed into a set of 50-mL centrifuge tubes containing 40 mL aliquots of 1 M HCl and the tubes shaken for 24 hrs to remove the Cd, Cu, and Pb adsorbed on the membrane. The desorption process was repeated once. Cadmium, Cu, and Pb in the solutions was determined by atomic absorption spectroscopy.

Extraction of soil-borne Cd, Cu, and Pb by resin membrane

Four-gram of soil (passed through 80 mesh), 40 mL of deionized water, and one piece of Ca-saturated Chelex resin membrane (5 cm²) in a PP bag were placed in a 50-mL centrifuge tube. The tubes were shaken for 24 hrs. The soil suspensions were decanted and the resin membrane was recovered, rinsed thoroughly with distilled water, and air-dried. It was then transferred into a clean 50-mL centrifuge tube and 40-mL aliquots of 1 M HCl were added. The tube was shaken for 24 hrs to remove the Cd, Cu, and Pb adsorbed on the membrane. The Cd, Cu, and Pb desorption procedures

were repeated once. The Cd, Cu, and Pb concentrations in the aliquots of 1 M HCl were determined by atomic absorption spectroscopy.

Cadmium, Cu, and Pb uptake by young seedlings of wheat

A modified Neubauer method (Lee, 1983) was used to determine plant-extractable Cd, Cu, and Pb of the soil. Fifty-five wheat seeds (*Triticum vulgare*, variety Taichung select No. 2) were placed evenly in a series of plastic bottles which were filled with the soil and acid-washed silica sand. The details of wheat cultivation were described by Lee and Zheng (1993). Each experimental treatment was triplicated. The experiment was carried out in a greenhouse at 26±10°C for 30 days. At the end of the experiment, seedlings including roots were washed free of silica sand and soil, oven-dried at 70–80°C for 48 hrs, ground to pass a 60-mesh sieve, and stored for analysis.

Extractable soil Cd, Cu, and Pb by other methods

The Cd, Cu, and Pb in soils were also extracted by 0.1 M HCl (Nelson et al., 1959), 0.01 M CaCl₂ (Whitten and Ritchie, 1991), DTPA (pH=7.3) (Lindsay and Norvell, 1978), and DTPA(pH=5.3) (Norvell, 1984) and the concentration of Cd, Cu, and Pb in the extracts were determined by atomic absorption spectroscopy.

Soil treatments

Four soils used in this study were selected from agricultural lands in Taiwan which were contaminated primarily due to irrigation with Cd, Cu, or Pb containing waste water discharged from chemical plants (Lee and Liao, 1990). Five uncontaminated soils which represented soils of the major agricultural areas in Taiwan were also used. The properties of these soils were summarized in Table 1. The soils varied widely in pH, texture, and CEC. To test the method's applicability to major soils of Taiwan, the four uncontaminated soils were treated with various levels of Cd, Cu, and Pb. The amounts of heavy metal addition for various treatments are shown in Table 2. Cadmium, Cu, and Pb were added as CdCl₂ · 2.5H₂O, CuCl₂ · 2H₂O, and Pb(NO₃)₂ solutions. The chemical forms of these metals were similar to those presented in industrial waste water in Taiwan. The treated soils underwent 3 wetting-drying cycles at room temperature. Following these treatments, the soils were ground, passed through a

Table 1. Physical and chemical properties of the soils studied

Soil series ^a	Classification	pH	Organic matter (%)	CEC (cmol (+) kg ⁻¹)	Texture	Free	Free
		H ₂ O				Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)
Pinchen (Pc)	Tropeptic Haploorthox	4.0	2.0	8.4	SiC	2.40	0.38
Jente (Je)	Haplaquept	5.3	2.2	6.4	L	0.63	0.09
Erhlin (Eh)	Haplaquept	6.5	2.6	9.1	SiCL	0.60	0.07
Chengchung (Cf)	Udifluvent	7.7	1.5	6.0	L	0.55	0.06
Taikang (Tk)	Fluventic Ustochrept	8.2	1.5	16.3	C	1.57	0.11
Chunghsing (Ce) ^b	Typic Paleudult	4.9	1.4	8.8	SiC	0.06	0.23
Tsaota (Ts) ^b	Typic Quartzipsamment	5.2	1.0	4.2	SL	0.47	0.10
Annei (An) ^b	Udifluvent	7.4	1.0	5.1	SL	0.74	0.11
Neuniaokang (YNn) ^b	Udifluvent	7.7	5.4	8.3	L	0.74	0.11

^a The letters in the parentheses represent the abbreviation of soil name.

^b Collected from contaminated agricultural soils.

Table 2. The amounts of heavy metal added into uncontaminated soils for various levels of treatments

Treatment level	Amounts of metal added (mg kg ⁻¹)		
	Cd	Cu	Pb
0	0	0	0
1	5	50	60
2	10	100	120
3	20	200	240

40-mesh sieve, mixed thoroughly, and stored for plant uptake experiments.

Results and discussion

Extraction conditions

The Ca-saturated Chelex membrane is effective in adsorbing Cd, Cu, and Pb from the solutions containing a mixture of metals and the adsorbed Cd, Cu, and Pb can also be effectively removed from the membrane by 1 M HCl. The recoveries of Cd, Cu, and Pb by the Ca-Chelex membranes reached 93, 100, and 100 %, respectively with 20 hrs of equilibration (Fig. 1). The

Fig. 1. The recovery of Cd, Cu, and Pb for 5cm² Ca-saturated Chelex resin membrane in 40 mL solution (Cd 2 mg L⁻¹, Cu 20 mg L⁻¹, and Pb 24 mg L⁻¹) as a function of time. (The error bar stands for $\pm 1SD$.)

high recovery rates by the Ca-saturated Chelex membrane for Cd, Cu, and Pb make the membrane suitable for extracting these three metals simultaneously. The extraction time was set at 24 hrs for all the experiments, as 20 hrs were sufficient for the Cd, Cu, and Pb adsorption to reach equilibrium. The cation exchange capacity of Ca-saturated Chelex membrane for divalent metal is above 8 $\mu\text{mol cm}^{-2}$ (Lee and Zheng, 1993). Five cm² of Ca-saturated Chelex membrane will pro-

Table 3. Dry matter weight and concentration of Cd, Pb, Cu in wheat seedlings grown in all tested soils with various treatments

Soil ^a	Dry matter weight (g/pot)	Concentration (mg kg ⁻¹)		
		Cd	Cu	Pb
Pc0 ^b	1.91 ± 0.04	ND ^c	50 ± 10	9 ± 8
Pc1	2.1 ± 0.3	18 ± 1	150 ± 70	5 ± 1
Pc2	2.1 ± 0.3	54 ± 5	230 ± 20	20 ± 10
Pc3	1.9 ± 0.1	180 ± 10	470 ± 40	60 ± 10
Je0	2.3 ± 0.1	ND ^c	60 ± 20	21 ± 5
Je1	2.3 ± 0.1	13 ± 1	80 ± 20	23 ± 7
Je2	2.7 ± 0.3	29 ± 4	220 ± 70	26 ± 5
Je3	3.0 ± 0.3	64 ± 7	410 ± 70	23 ± 6
Eh0	2.4 ± 0.2	ND ^c	40 ± 10	15 ± 6
Eh1	2.4 ± 0.1	17 ± 3	46 ± 5	17 ± 4
Eh2	2.4 ± 0.2	29 ± 3	80 ± 10	23 ± 3
Eh3	2.5 ± 0.1	28 ± 1	110 ± 30	28 ± 6
Cf0	2.5 ± 0.2	ND ^c	70 ± 20	9 ± 5
Cf1	2.5 ± 0.1	7 ± 1	76 ± 3	15 ± 8
Cf2	2.58 ± 0.07	14 ± 1	100 ± 20	17 ± 5
Cf3	2.52 ± 0.06	30 ± 3	160 ± 10	28 ± 7
Tk0	1.8 ± 0.2	ND ^c	70 ± 10	12 ± 2
Tk1	1.88 ± 0.08	8 ± 1	60 ± 10	10 ± 7
Tk2	1.99 ± 0.03	15 ± 1	80 ± 10	13 ± 5
Tk3	1.90 ± 0.03	23 ± 1	110 ± 10	22 ± 6
Ce	2.2 ± 0.1	65 ± 2	35 ± 4	10 ± 10
Ts	2.3 ± 0.1	30 ± 3	35 ± 2	23 ± 8
An	2.3 ± 0.2	ND ^c	120 ± 10	4 ± 1
YNn	2.1 ± 0.1	160 ± 20	90 ± 40	280 ± 10

^a The number following the abbreviation of soil name is the level of heavy metal added.

^b For amount of heavy metal added see Table 2.

^c < Detection limit (0.05 mg kg⁻¹)

vide exchange sites for at least 40 μ mol divalent metal which is sufficient for Cd, Cu, and Pb released from 4 g of heavily heavy metal-contaminated soils.

Plant uptake of Cd, Cu, and Pb

The dry matter yields and Cd, Cu, and Pb concentrations of wheat seedlings grown in soils with various treatments are presented in Table 3. The dry matter yields are not significantly different (at $p < 0.05$) between the treatments. The growth of wheat seedlings was not inhibited by the Cd, Cu, and Pb in the soils, thus the total uptake of Cd, Cu, and Pb by wheat seedlings could be used to represent phytoavailability of Cd, Cu, and Pb in the soils.

Table 4. Correlation coefficients between Cd, Cu, and Pb uptake by wheat and those extracted by various methods

Extraction method	Cd	Cu	Pb
0.1 M HCl	0.61**	0.60**	0.98***
0.01 M CaCl ₂	0.93***	0.69***	0.06
DTPA (pH 7.3)	0.64***	0.71***	0.98***
DTPA (pH 5.3)	0.63***	0.52**	0.99***
Chelex resin membrane	0.86***	0.82***	0.80***

*** Significant at 0.1 % level

** Significant at 1 % level

Extractable soil Cd by resin membrane +vs. other methods

The correlations between Cd uptake by wheat seedlings and amounts of Cd extracted by all of the extraction methods were significant at $p < 0.01$ (Table 4). The correlation coefficients were all larger than 0.61. However, the strongest correlation of Cd uptake was with 0.01 M CaCl₂ extracted soil Cd ($r=0.93$), and the next highest was with resin membrane extracted Cd ($r=0.86$). Resin membrane extractable-soil Cd, according to the correlation coefficients, was a better indicator of plant available Cd than Cd extracted by DTPA ($r=0.64$) and 0.1 M HCl ($r=0.61$) extraction methods.

Extractable soil Cu by resin membrane vs. other methods

The correlations between Cu uptake by wheat seedlings and Cu extracted by all of the extraction methods we tested were significant at $p < 0.01$ (Table 4). Resin membrane extractable-soil Cu however had the strongest correlation with plant uptake Cu ($r=0.82$) and therefore, according to the correlation coefficients, was a better indicator of plant available Cu than Cu extracted by the other extraction methods ($r=0.52$ – 0.71) we tested.

Extractable soil Pb by resin membrane vs. other methods

The correlations between Pb uptake by wheat seedlings and Pb extracted by all of the tested extraction methods we tested ($r=0.80$ – 0.99) except the 0.01 M CaCl₂ extraction method ($r=0.06$) were significant at $p < 0.01$ (Table 4).

When the phytoavailability of Cd, Cu, and Pb in the soil were considered separately using the extraction methods we tested, only the plant uptake of Cu was better correlated statistically with Cu extracted by the Chelex resin membrane than with Cu extracted by other diagnostic methods. However, when the phytoavailability of Cd, Cu, and Pb of soil were evaluated collectively, the Cd, Cu and Pb extracted by the resin membrane were overall better indices of plant available Cd, Cu, and Pb than those extracted by other extraction methods we tested (Table 4). In addition, the resin membrane might be regenerated and used repeatedly. The membranes after metal extraction might be easily stored for later analysis or sent to centralized locations for metal determination, if necessary. In view of these advantages, the chelating resin membrane method is well suited to evaluate the quantities of plant-available Cd, Cu and Pb in soils.

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