DETERMINATION OF HEAVY METAL CONTAMINATION IN THE SOIL ENVIRONMENT USING ION EXCHANGE MEMBRANES

J. Liang and J.J. Schoenau, University of Saskatchewan, Sask., Saskatoon.

ABSTRACT

An anion exchange resin membrane saturated with chelating agent (AEM-DTPA) was used to assess the bioavailability of four heavy metals, Cd, Cr Ni and Pb via direct in soil burial. Two soils with four contamination rates of each metal were tested using three crops: oats, radish and lettuce. The resin membrane was buried in saturated soil with deionized water for 60 min. and extractable metals from the soils were correlated with uptake by plants grown in the soils. The amounts of heavy metals extracted by AEM-DTPA were significantly correlated with plant uptake and with metal extracted by the conventional DTPA method. The critical levels of the four heavy metals varied from crop to crop, and soil to soil. It was demonstrated that AEM-DTPA direct in-soil burial is a suitable method in assessing relative heavy metal bioavailability in polluted soil environments. It is a simple and easy to use procedure which reduces soil handling.

Index Words: Heavy metal, bioavailability, resin membrane, soil test, burial in-situ.

INTRODUCTION

Ion exchange resins in bead form have been used in assessing plant available nutrients for decades (Amer et al., 1955). Ion exchange resin in membrane form was first used by Saunders (1964). He found that the anion exchange membrane could be used to predict phosphorus availability in soil as well as resin in the bead form. Later on, the resin membrane technique was developed for soil testing for phosphorus availability (Sibbesen, 1978; Schoenau and Huang,1991) and as a multi-element soil test. More recently, this method has been developed into a routine soil test for macro-nutrient availability (Qian et al., 1992; Skogley, 1992).

However, no known studies have used ion exchange membranes to evaluate the availability of metals and other trace elements in soil. Recently, there has been much concern about the accumulation in soil of heavy metals such as Cd, Cr, Ni and Pb. Assessment of heavy metal pollution can be approached by assessing the degree of soil or crop pollution, and subsequentially predicting the likely effect on plant and animal health. Dilute acids, chelating agents, and neutral salts have been commonly used to extract metals from soils. Unfortunately, none of the existing methods are suitable for all metals and all situations. Ion exchange membranes saturated with chelating agents and buried in the natural soil environment may have a selective ability to adsorb metal ions, and mimic the action of plant roots. Development of such methods could permit environmental monitoring for predicting the potential toxicity and mobility of heavy metals for a wide range of soil types and metals. The objective of this study, therefore, was to develop a methodology for use of resin membranes to predict heavy metal bioavailability and toxicity in soil environment

MATERIALS AND METHODS

A growth chamber experiment was carried out to provide information on the relationship between the extractable levels of heavy metals in the soil, and uptake of these metals by oats (cereal), radishes (root crop) and lettuce (leafy vegetable) and their toxicity to the plant. Two soils were collected from the Saskatchewan agricultural region to represent a light (sandy loam) and heavy (clay) textured soil with low levels of the heavy metals concerned (Table 1). Soil samples collected from the field were air-dried, and passed through a 2-mm poly-ethylene sieve. The air-dried soil was spiked with metal in solution form, air-dried again, and then mixed in a mixing machine for 0.5 hours. The well mixed sample was then watered to field capacity, and incubated for two months before potting.

Table 1. Some properties of the two soils used as growth media.

Soil	pH	O.M	CEC	Clay	Total content (mg kg^{-1})			
	(1:2)	(%)	cmol kg^{-1}	(%)	Cd	Cr	Ni	Pb
Sandy loam	7.5	2.3	14.6	8.9	0.25	21.7	8.3	4.8
Clay	8.3	3.0	34.7	44.6	0.45	46.8	27.2	19.3

The experiment was a factorial design, with four levels of each metal: 0, 5, 10, 20 $\mu g\ g^{-1}$ added Cd, and 0, 40, 80, 160 $\mu g\ g^{-1}$ added Cr, Ni, and Pb. Each treatment was replicated three times. Five hundred grams of spiked soil was placed in a plastic pot. Eight oat seeds (Cascade) and 5 radish (Cherry Bell) and lettuce (Slobolt) seeds were seeded into each pot and thinned to 4 plants for oat, 3 plants for radish and 1 plant for lettuce after establishment of the seedling. Macro- and micro-nutrients were added to each pot to ensure that nutritional deficiency did not hinder plant growth. The growth chamber temperature was set at 25°C daytime and 12°C at night. Oats were allowed to grow to maturity, radish for 30 days and lettuce for 40 days. The harvested plant materials were dried at 60°C for one week and weighed for dry matter yield determination. The ground plant samples were digested using the wet ashing technique (H_2O_2/H_2SO_4) and determined by AAS for heavy metal concentration.

Soil analyses prior to metal spiking included: pH in 1:1 soil to water suspension; organic carbon by a modified Walkley-Black procedure; exchangeable bases by equilibration with 1 M NH_4OAc and particle size analysis by the pipette methods; total soil metal content using the microwave dissolution procedure; DTPA-extractable metals by the method of Lindsay and Norvell (1978).

AEM-chelate burial (membrane) procedure: Strips of anion exchange membrane (AEM) (6 cm x 2 cm, B.D.H. product no. 55164) were placed in a 0.01 M DTPA + 0.02 M NaOH solution to saturate the positively charged functional groups on the membrane with DTPA. The strips were then washed with deionized water and then buried into 70 grams of soil in a plastic vial. The soil was saturated with deionized water and the buried membranes were allowed to sit for 60 min.. Then the membrane strips were removed from soil, and washed free of soil with deionized water. The membrane was then shaken with 20 mL of 1 N HCl for 2 hours. The metal content in the 1 N HCl eluents was determined by AAS. This procedure may be used in the field directly. The membranes are reusable and are made ready for reuse by washing again in the DTPA solution.

RESULTS

Cadmium

Effect of enhancement of 'available' cadmium level

Both DTPA and membrane extractable Cd reflected the relative Cd contamination of soil very well, and acted as a suitable index of relative Cd bio-availability (Table 2). Added Cd had no significant effect on yield of radish and oats, over the

Table 2. Effect of added Cd as $CdSO_4$ on DMY of radish, lettuce and oats (average of three pots).

	Spike rate (mg kg^{-1})			
	0	5	10	20
	Sandy loam soil			
DTPA-Cd (mg kg^{-1})	0.1	3.9	6.9	16.1
Membrane Cd (µg/10 cm^2)	0.1	0.4	0.7	1.3
DMY(g)/radish	2.8_a	2.4_a	2.5_a	2.5_a
DMY(g)/lettuce	3.5_a	2.2_b	1.7_{bc}	1.3_c
DMY(g)/oats	15_a	15_a	13_b	14_{ab}
	Clay soil			
DTPA-Cd (mg kg^{-1})	0.1	4.4	8.0	17.9
Membrane Cd (µg/10 cm^2)	0.1	0.4	0.8	1.4
DMY(g)/radish	3.0_a	2.7_a	3.1_a	3.4_a
DMY(g)/lettuce	4.0_a	3.2_{ab}	2.6_b	1.5_c
DMY(g)/oats	15_a	15_a	15_a	14_a

Values followed by a different letter are significantly different at $p = 0.05$ for each crop.

range employed. Addition of 5 mg kg^{-1} Cd significantly inhibited the growth of lettuce in the sandy loam soil, while a spike rate of 10 mg kg^{-1} was enough to reduce yield in the clay soil. These results confirm the findings that leafy vegetable are more sensitive to Cd toxicity than cereals or root crops

Effectiveness of DTPA and membrane burial in predicting Cd uptake

Cadmium uptake by radish and oats, as well as Cd concentration was significantly correlated with spike rate (Table 3). This suggests that Cd can be readily taken up by plants to produce quite high concentrations in the plant without the appearance of phytotoxicity, so that an apparently normal crop may be unsafe for human and animal consumption. The regression coefficients in Table 3 demonstrate that membrane extractable Cd can predict Cd bioavailability similar to the conventional DTPA method.

Table 3. Coefficient of determination (r^2) for relationship between Cd in plant and Cd added rate, DTPA-Cd,and membrane-Cd.

	Added rate	DTPA-Cd	Membrane-Cd
Cd in plant	r^2	r^2	r^2
Radish uptake	0.988*	0.986*	0.989*
Lettuce conc.	0.980*	0.986*	0.980*
Oat uptake	0.985*	0.989*	0.994**

*, **, Significant at the 0.05, 0.01 levels, respectively.

Chromium

Effect of added Cr on plant dry matter yield

Both conventional DTPA- and membrane extractable Cr reflect the Cr spiking very well (Table 4). In this experiment, the highest treatment level (160 mg kg^{-1}), corresponding to determined levels of DTPA-extractable Cr of greater than

Table 4. Effect of added Cr as $CrCl_3$ on dry matter yield of radish, lettuce and oats (average of three pots).

	Spike rate (mg kg^{-1})			
	0	40	80	160
	Sandy loam soil			
DTPA-Cr (mg kg^{-1})	0.01	0.11	0.17	0.34
Membrane-Cr (µg/10cm^2)	0.00	0.09	0.21	0.39
DMY(g)/radish	2.8_a	3.0_a	3.2_a	2.1_b
DMY(g)/lettuce	3.5_a	2.7_a	2.7_a	1.4_b
DMY(g)/oats	15_a	15_a	16_a	13_b
	Clay soil			
DTPA-Cr (mg kg^{-1})	0.01	0.06	0.08	0.12
Membrane-Cr (µg/10cm^2)	0.00	0.10	0.17	0.35
DMY(g)/radish	3.0_a	3.0_a	3.5_a	3.5_a
DMY(g)/lettuce	4.0_a	3.4_a	3.2_a	3.7_a
DMY(g)/oats	15_a	15_a	15_a	15_a

Values followed by a different letter are significantly different at $p = 0.05$ for each crop.

0.3 mg kg^{-1} and of membrane Cr of greater than 0.4 µg/10cm^2, produced a significant yield reduction in the three crops grown in the sandy loam soil. However, no significant effects were observed on yield of these three crops grown in the clay soil over the range of Cr rate employed.

Effectiveness of DTPA and membrane burial in predicting Cr bioavailability

Radish Cr uptake and lettuce Cr concentration are significantly correlated with Cr spike rate, DTPA-extractable and membrane Cr in the sandy loamsoil (Table 5). Generally, both the conventional DTPA method and the membrane burial method predict Cr bioavailability for radish and lettuce very well.

Table 5. Coefficient of determination (r^2) for relationship between Cr in plant and Cr added rate, DTPA-Cr, and membrane-Cr in the sandy loam soil.

	Added rate	DTPA-Cr	Membrane-Cr
Cr in plant	r^2	r^2	r^2
Radish uptake	1.00***	0.995**	0.998***
Lettuce conc.	0.997**	0.998***	0.987*
Oats straw conc.	0.915	0.965*	0.977*

*, **, ***, Significant at the 0.05, 0.01, 0.001 levels, respectively.

Nickel

Effect of added Ni on plant dry matter yield

The DTPA- and membrane extractable Ni represent the rate of Ni application very well (Table 6). Dry matter yield response to spiked Ni varied widely from crop to crop, and soil to soil. Lettuce is more sensitive than the other crops with lettuce dry matter declining with increasing Ni spike rate on both soils, the decline starting at rates above 40 mg kg^{-1}. Dry matter yield of radish and oats declined only at the highest treatment level in the sandy loam soil.

Table 6. Effect of added Ni as $NiSO_4$ on dry matter yield of radish, lettuce and oats (average of three pots).

	Spike rate (mg kg^{-1})			
	0	40	80	160
	Sandy loam soil			
DTPA-Ni (mg kg^{-1})	0.9	32.5	63.4	139.4
Membrane-Ni (µg cm^{-2})	0.01	2.4	4.5	11.0
DMY(g)/radish	2.8_a	2.9_a	2.6_a	0.3_b
DMY(g)/lettuce	3.5_a	2.5_b	2.2_b	0.2_c
DMY(g)/oats	15_a	15_a	14_{ab}	11_b
	Clay soil			
DTPA-Ni (mg kg^{-1})	2.0	23.2	54.8	96.2
Membrane-Ni (µg cm^{-2})	0.02	1.2	2.6	5.0
DMY(g)/radish	3.0_a	3.1_a	3.6_a	3.3_a
DMY(g)/lettuce	4.0_a	3.2_{ab}	2.6_{bc}	2.1_c
DMY(g)/oats	15_a	15_a	15_a	14_a

Values followed by a different letter are significantly different at $p = 0.05$ for each crop.

Effectiveness of DTPA and membrane burial in predicting Ni bioavailability

Nickel uptake by radish and lettuce and Ni concentration in oat grain increased linearly with Ni spike rate, DTPA-extractable and membrane Ni (Table 7). Both DTPA-extractable and membrane burial can predict plant Ni uptake or concentration very well. It can be concluded that ion exchange membrane burial is a good predictor for Ni bioavailability.

Table 7. Coefficient of determination (r^2) for relationship between Ni in plant and Ni added rate, DTPA-Ni, and membrane-Ni in the sandy loam soil.

	Added rate	DTPA-Ni	Membrane-Ni
Ni in plant	r^2	r^2	r^2
Radish uptake	1.00***	1.00***	1.00***
Lettuce uptake	1.00***	1.00***	1.00***
Oats grain conc.	0.986*	0.985*	0.979*

*, ***, Significant at the 0.05, 0.001 levels, respectively.

Lead

Effect of added Pb on plant dry matter yield

Both soil availability indices, DTPA and membrane burial, reflect Pb spike rate (Table 8). No obvious deleterious effects on the growth of radish, lettuce and oats were observed where soluble Pb was added up to a level of 160 mg kg^{-1} in the clay soil. Plants do not tend to accumulate Pb. This confirms the find-ings that only a small proportion of the Pb in soil is available for uptake by plants. Lead uptake by the three crops was not significantly correlated with Pb spike rate, DTPA-extractable and membrane Pb (data not shown). Only the lettuce Pb concen-tration was significantly correlated with DTPA-extractable and membrane Pb. This suggests that the relationship between lead contamination of soil and plant uptake is weak.

Table 8. Effect of added Pb as $PbCl_2$ on dry matter yield of radish, lettuce and oats.

	Spike rate (mg kg^{-1})			
	0	40	80	160
	Sandy loam soil			
DTPA-Pb (mg kg^{-1})	0.5	30.6	64.7	113.1
Membrane-Pb (μg cm^{-2})	0.02	2.6	4.8	8.7
DMY(g)/radish	2.8$_{ab}$	3.2$_a$	2.8$_{ab}$	2.3$_b$
DMY(g)/lettuce	3.5$_a$	3.0$_{ab}$	3.0$_{ab}$	2.3$_b$
DMY(g)/oats	15$_a$	15$_a$	16$_a$	15$_a$
	Clay soil			
DTPA-Pb (mg kg^{-1})	1.5	33.2	61.3	106.4
Membrane-Pb (μg cm^{-2})	0.14	2.9	6.4	11.4
DMY(g)/radish	3.0$_a$	2.5$_a$	3.2$_a$	2.6$_a$
DMY(g)/lettuce	4.0$_a$	3.1$_a$	3.2$_a$	2.9$_a$
DMY(g)/oats	15$_a$	15$_a$	15$_a$	14$_a$

Values followed by a different letter are significantly different at $p = 0.05$ for each crop.

SUMMARY

This study describes the development of a methodology for evaluating the bioavailability of heavy metals in soil environments. Ion exchange membranes saturated with chelated agents can be buried in situ to simulate the action of plant roots. Membrane burial will measure the metal cation pools as well as the diffusion to the sink and is a simple and easy to use procedure. Nickel and Cd are more toxic to plant growth than Cr and Pb. Leafy vegetables are more sensitive to heavy metal toxicity and the toxic effects are pronounced in soils with low cation exchange capacity. Plants do not tend to accumulated Pb while Cd can be readily taken up by plants.

ACKNOWLEDGEMENTS

The research was supported by Saskatchewan Environmental Technology Development, Saskatchewan Environment and Public Safety Fund.

REFERENCES

Amer, F., D.R. Bouldin, C.A. Black and F.R. Duke. 1955. Characterization of soil phosphorus by anion exchange resin adsorption and ^{32}P equilibration. Plant and Soil 6:391-408.

Lindsay, W.L., and W.A. Norvell. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42: 421-428.

Qian, P., J.J. Schoenau and W.Z. Huang. 1992. Use of ion exchange membranes in routine soil testing . Comm. Soil Sci. Plant Anal. 23: 1791-1840.

Saunders, W.M.H. 1964. Extraction of soil phosphate by anion-exchange membrane. N.Z. J. Agr. Res. 7: 427-431.

Schoenau, J.J. and W.Z. Huang. 1991. Anion-exchange membrane, water, and sodium bicarbonate extractions as soil tests for phosphorus. Comm. Soil Sci. Plant Anal. 22: 465-492.

Sibbesen, E. 1978. An investigation of the anion-exchange resin method for soil phosphate extraction. Plant and Soil 50: 305-321.

Skogley, E.O. 1992. The universal bioavailability environment/soil test unibest. Commun. Soil Sci. Plant Anal. 23: 2225-2246.