AMELIORATION OF Cd CONTAMINATED AGRICULTURAL SOILS USING CATION EXCHANGERS.

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ABSTRACT

In Australia extensive areas of agricultural soils have been contaminated with Cd as a result of the repeated use of high-Cd phosphate fertilizers. The degree of contamination is sufficiently great in some areas that food crops grown on these soils contain unacceptably high Cd concentrations. Glasshouse lettuce (*Latuca sativa* cv. Cos) growth trials were conducted to assess the potential for remediation of Cd contaminated agricultural soils using a novel high-charge cation exchange material, produced by the delamination of kaolinite. This material, named kaolin amorphous derivative (KAD), has a CEC of ≈ 200 $cmol_{(+)}$/kg and a high selectivity for Cd. A second exchanger, Ca-clinoptilolite with a CEC of ≈ 160 $cmol_{(+)}$/kg was also evaluated. For the three soils tested, KAD application, at the equivalent of 2.5 t/ha, reduced plant tissue Cd concentration by ≈ 30%. Application of zeolite at the same rate (2.5 t/ha), or KAD at 250 kg/ha did not significantly reduce the tissue Cd concentration

INTRODUCTION

Cadmium (Cd) has no known biological function, but has long been recognized as a toxic heavy metal in industrial situations. During the 1950's and 1960's concern began to be expressed over possible effects on human health of long-term exposure to low concentrations of Cd, particularly as a contaminant in food. Australian scientists, Williams and David (1973) were among the earliest to establish linkages between Cd impurities in fertilizers and the accumulation of Cd in soils and food crops. This in part reflects the large P inputs typically required to achieve production on Australian soils and the relative high Cd concentration in the rock phosphates used to manufacture Australian phosphate fertilizers. By 1988, it was clear, particularly in southern Australia, that Cd was accumulating to unacceptable concentrations in some animal and plant products (Rothschild 1988). This paper describes the preliminary evaluation of a novel cation exchange material's effectiveness as an ameliorant for Cd contaminated soils.

MATERIALS AND METHOD

Characterization of ameliorants

Delamination of kaolinite by heating under alkaline conditions produces a material with high surface area and surface charge density (kaolin amorphous derivative - KAD). The characteristics of the material produced can be altered by modifying the reaction conditions. The KAD used in this study was produced by reaction with KOH, and hence the cation exchange capacity (CEC) is K^+ saturated. It was selected because of its high affinity for metals, though its particularly high affinity for Cu raised concerns for the supply of Cu to plants. The zeolite used was a Ca-saturated clinoptilolite ground to pass a 0.25 mm sieve.

The affinity of the exchangers for Cd and Cu was evaluated by determining adsorption curves in a manner analogous to that commonly used for phosphate (Fox and Kamprath 1970). Prior to the assessment of adsorption on KAD, the exchange sites were saturated with Ca by repeated washing with 1 M $Ca(NO_3)_2$ solution, and the pH adjusted to 7.0. This condition was considered to be a better representation of the field situation where K^+ is likely to be removed from the exchange by plant uptake and competition from Ca^{2+}. A period of seven days equilibration was used following addition of Cd or Cu as nitrate salts, then the concentration of Ca and Cd, or Cu, in the supernatant was determined by inductively coupled plasma atomic absorption spectroscopy (ICP-AES), and the amount of metal adsorbed and Ca displaced calculated.

The CEC of the ameliorants was evaluated using NH_4^+ as an index cation. Exchange sites were saturated by overnight shaking with 1 M NH_4Cl, followed by three washes with 0.2 M NH_4Cl. Ammonium was displaced by 1M KCl and determined by distillation and titration. This result was corrected for entrained 0.2 M NH_4Cl to provide a measurement of the CEC.

Plant growth study
A glasshouse lettuce (*Lactuca sativa* cv. Cos) growth trial was conducted to assess the effect of cation exchange ameliorants on the bioavailability of Cd in three sandy loam soils from the Bundaberg region in central Queensland, Australia. The soils were used at their field pH, and following the addition of lime ($CaCO_3$) or HCl to achieve three pH values (1:5 soil:water) ranging from 4.5 to 6.5. The two cation exchange ameliorants, zeolite applied at 2.5 t/ha and KAD applied at 2.5 t/ha and 0.25 t/ha, were mixed throughout the soil mass before planting. Residual alkalinity present in the KAD was neutralized by titration to pH 7.0 with HCl. Basal nutrients (N 100 kg/ha, P 100 kg/ha, Mg 40 kg/ha, Mn 1.25 kg/ha, Cu 4 kg/ha, Zn 4 kg/ha) were applied to all pots, with K (40 kg/ha) applied to treatments receiving no, or low, KAD applications. Pots were maintained close to field capacity (10 kPa suction) by daily applications of deionized water. Plants were harvested 55 days after sowing, oven dried to constant weight at 75°C and the dry matter produced recorded. Plant material was finely ground and a subsample digested using nitric/perchloric acid and analyzed for Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn by ICP-AES, and for Cd by inductively coupled plasma mass spectrometry (ICP-MS).

Soil solution was extracted by centrifuge drainage, the pH was determined, then solutions were filtered to 0.025 µm and elemental composition determined by ICP-MS.

All data was analyzed using analysis of variance, and significant differences identified using least significant difference (LSD) tests. Statistical analysis calculations were made using SAS programs (Anon 1996).

RESULTS AND DISCUSSION

The use of a cation exchanger as an ameliorant for Cd contaminated soils is based on the exchange complex "capturing" the metal and in this manner lowering its concentration in soil solution. To be effective as an ameliorant, the affinity of the exchange complex for Cd must be greater than its affinity for the major cations present in soil solution. The KAD showed a high affinity for both metals, though the preference for Cu over Cd was pronounced at the low concentrations likely to be encountered in soil solutions (Figure 1.). At low concentrations, removal of Cu and Cd from solution was not matched by a corresponding increase in solution Ca concentration, indicating that adsorption (rather than exchange) was responsible for the reduction in solution Cu and Cd concentration. At solution metal concentrations of > 10 mg/L, Cu and Cd removal from solution was approximately balanced by a increase in Ca concentration, indicating an exchange reaction. Zeolite showed a lower affinity for Cu or Cd than the KAD.

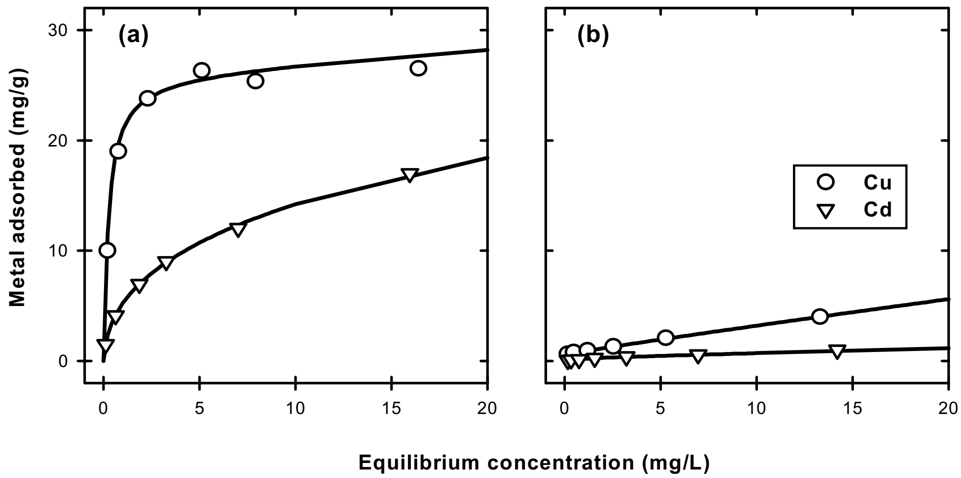

Figure 1. Adsorption curves for Cu and Cd on (a) KAD and (b) Clinoptilolite from a 0.01 M $CaCl_2$ matrix.

Application of KAD or zeolite did not significantly (p>0.05) alter the dry matter yield in most soils, as the level of Cd contamination was not sufficiently high to limit plant growth (Table 1). The exception was (soil 3+acid) where soil acidity limited plant growth and the small liming effect of the high rate of KAD increased plant growth (Table 2). This treatment (soil 3+acid) was not considered further.

Table 1. The effect of KAD and zeolite treatments on lettuce dry matter yield (g/pot).

	Soil 1			Soil 2			Soil 3		
	+ acid		+ lime	+ acid		+ lime	+ acid		+ lime
Control	3.64	4.36	4.05	3.89	3.99	4.52	0.56[a]	5.01	5.36
KAD 0.25 t/ha	4.24	4.51	4.51	4.05	4.54	4.47	0.94[a]	5.45	5.41
KAD 2.5 t/ha	3.93	4.35	4.02	4.11	3.21	4.52	2.29[b]	5.35	5.38
Zeolite 2.5 t/ha	4.72	4.19	3.97	4.02	4.02	4.18	1.07[ab]	4.78	5.31

* Numbers in a column with the same superscript letter are not significantly different (P<0.05)

Table 2. The effect of KAD and zeolite treatments on soil solution pH.

	Soil 1			Soil 2			Soil 3		
	+ acid		+ lime	+ acid		+ lime	+ acid		+ lime
Control	4.07	5.33	6.41	4.92	5.21	6.22	3.59	4.48	5.00
KAD 0.25 t/ha	4.12	5.63	6.25	4.95	5.37	6.18	3.64	4.44	4.99
KAD 2.5 t/ha	5.05	5.50	6.46	4.85	5.85	6.20	4.09	5.09	5.38
Zeolite 2.5 t/ha	4.07	5.27	6.23	4.90	5.38	6.22	3.58	4.54	5.12

Plant tissue Cd concentration was significantly (P<0.05) lowered by KAD application at 2.5 t/ha in all soils. Reductions ranged from 19 % to 43% of the Cd content of the control. Reduced tissue Cd content is attributed to adsorption of Cd by the KAD material, rather than to an effect of the higher pH in these treatments. This contention is supported by the observation that the application of lime did not markedly reduce the plant tissue Cd concentration in any of the soils used. Failure of liming to reduce plant Cd uptake has been observed in a number of situations (McLaughlin *et al*. 1996), and may be attributed to displacement of Cd into soil solution by Ca.

Table 3. The effect of KAD and zeolite treatments on lettuce shoot Cd concentration (mg/kg).

	Soil 1			Soil 2			Soil 3		
	+ acid		+ lime	+ acid		+ lime	+ acid		+ lime
Control	3.34[a*]	3.29[a]	3.25[a]	3.59[a]	3.51[a]	3.60[a]	6.70[a]	2.29[a]	2.32[a]
KAD 0.25 t/ha	3.11[ab]	2.77[a]	3.11[a]	3.48[a]	3.28[a]	3.61[a]	7.26[a]	1.88[b]	1.99[ab]
KAD 2.5 t/ha	2.34[b]	2.17[b]	2.63[b]	2.63[b]	2.73[b]	2.85[b]	4.36[b]	1.73[b]	1.46[b]
Zeolite 2.5 t/ha	3.40[a]	2.79[a]	3.41[a]	3.33[a]	3.37[a]	3.77[a]	6.55[a]	2.32[a]	2.41[a]

* Numbers in a column with the same superscript letter are not significantly different (P<0.05)

The plant tissue Cu concentration was not significantly (P<0.05) altered by the addition of the cation exchangers. However, tissue Mg, Na, Mn and Zn concentrations were significantly (P<0.05) lowered and tissue K concentration significantly (P<0.05) increased by KAD addition at both rates of application (data not presented).

REFERENCES

Anon. SAS/STAT software. Release 6.12 Cary, NC: SAS Institute Inc. 1996.

Fox RL, Kamprath EJ (1970), Soil Sci. Soc. Am. Proc. 34:902-907.

McLaughlin MJ, Tiller KG, Hamblin A. (1996), In: Fertilizers as a Source of Cadmium. Paris, Organization for Economic Co-operation and Development, pp.189-217.

Rothschild GHL (1988), In: Cadmium Accumulations in Australian Agriculture: National Symposium Canberra 1-2 March 1988. (J Simpson, W Curnow, Editors) Department of Primary Industries and Energy, Bureau of Rural Resources, Proceedings No. 2. Canberra, Australian Government Publishing Service, pp. iii

Williams CH, David DJ (1973), Aust. J. Soil Res. 11:43-56.