Cadmium-copper competitive sorption in soils*

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INTRODUCTION. — Wastewaters of municipal and industrial origin used to irrigate farmlands contain heavy metals which are sorbed on the surfaces of soil particles. Among those metals are cadmium (Cd) and copper (Cu). The degree to which each of these metals reacts independently or compete with each other for similar sorption sites can influence the retention of each other in the surface of the soil profile and/or its migration and distribution through the soil profile or leaching to groundwater.

The extent of sorption of Cd and Cu in soils has been reported in a number of studies including those of CAVALLARO and MC BRIDE (1978), ELLIOTT *et al.* (1986), King (1988a; 1988b), KUO and BAKER (1983), KURDI and DONER (1983), and LEHMAN and HARTER (1984). Not many papers, however, have reported the competitive sorption of heavy metals in soils of various characteristics. Heavy metal sorption is probably a function of numerous factors such as clay content and type, organic matter, oxides and soluble salts. However, the soil properties more significantly affecting sorption at trace levels are, according to CAVALLARO and MC BRIDE (1978), not well defined. More recent work by ELLIOTT *et al.* (1986) has shown that the type of organic matter can play an important role in heavy metal sorption.

The objective of this study was to determine the sorption of Cd and Cu with and without the presence of the other to establish the competitive sorption by soils of different properties.

MATERIAL AND METHODS. — The soil samples used in this study were collected from the 30- to 60-cm depth of four soil profiles of Chile; Osorno and Frutillar soils are Andepts and the Encinas and Casas soils are Xerocrepts. The Encinas and Casas soils are located in a semi-arid region (less than 350 mm of rainfall per year) and are irrigated with untreated

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mixed domestic and industrial wastewaters from the City of Santiago. The Osorno and Frutillar are located in a temperate high-rainfall region (more than 1800 mm per year) and which might eventually be affected by the deposition of industrial wastes containing metals. The Xerocrepts have mostly montmorillonite clays, whereas the dominant clay in the Andepts is allophane.

The air-dried soils were crushed and passed through a 2-mm non-metallic sieve. Soil organic carbon (C) was determined by the Walkley-Black method (NELSON and SOMMERS, 1982). The cation-exchange capacity (CEC) was determined by the NaOAc procedure (RHOADES, 1982). For the Cd-sorption studies 1-g samples of each soil were treated with 40-ml aliquots of $Cd(C10_4)_2$ solutions containing 1.8, 9.4, 15.7, 24.2, 38.8 and 53.8 micromoles of Cd, respectively. The suspensions of soil in these solutions were shaken for 24 hrs at room temperature (20 ± 2C) after which they were centrifuged and the Cd in the clear supernatant was determined using atomic absorption spectrophotometry. Duplicate suspensions were used for each treatment. To determine the effect of Cu on Cd sorption, one set of samples was treated with 27 micromoles of $Cu(C10_4)_2$ with treatments of 2.5, 8.4, 20.0, 34.1, 47.0 and 57.1 micromoles of Cd, respectively, using the same amount of soil and solution.

For the Cu-sorption studies the same procedures were used, adding 2.3, 10.8, 23.0, 25.4, 44.4, and 53.6 micromoles of $Cu(C10_4)_2$, respectively. To determine the effect of Cd on Cu sorption, 25 micromoles of Cd were included with each $Cu(C10_4)_2$ addition of 2.2, 10.5, 20.1, 30.0, 45.2 and 58.0 micromoles.

In all experiments, the pH of the soil suspension was measured at 0.5 hr and 24 hr following the addition of metal perchlorates.

A separate estimate of competition between Cd and Cu was obtained by adding a constant amount of Cd plus Cu at 10 micromoles per g of soil with the mole ratio for each cation ranging from 0.1 to 1.0. The cations were added in 25 ml of solution to 1.0 g samples of soil. The resultant suspensions were shaken for 24 hrs after which they were centrifuged and samples of the clear supernatant were analyzed for Cd and Cu.

RESULTS AND DISCUSSION. — Data for pH of the saturated paste, CEC and adsorption maxima, for non-competitive adsorption experiments, calculated from the Langmuir equation, are presented in Table 1. The linear correlation coefficients for the relationships between C/x/m and C in the equation $c/x/m = 1/kd + C/d$ in which C is the concentration in solution, x is the amount of metal sorbed, m is the amount of soil, k is the bonding energy constant and d is the adsorption maximum, were highly significant ($r = 0.938$ or greater). The adsorption maxima for Cu was slightly greater than that for Cd for the Xerocrepts, but slightly smaller for the

TAB. 1. — *Data for pH, organic C content, CEC, and the adsorption maximum calculated from the Langmuir equation.*

Soil	pH	Organic C	CEC	Adsorption Maxima Cd	Adsorption Maxima Cu
		%	cmol kg^{-1}		
Encinas	7.4	0.43	16.8	4.1	5.1
Casas	7.2	0.39	16.7	5.2	5.4
Frutillar	5.5	1.56	30.2	2.5	1.9
Osorno	5.7	5.75	26.8	2.8	2.0

Andepts. The adsorption maxima for each cation was much greater in the Xerocrepts than in the Andepts, but the ratio for Xerocrepts to Andepts for Cd was 1.8, whereas it was 2.6 for Cu, indicating that the effects of differences in soil properties were greatest with Cu. The differences in adsorption maxima between the Xerocrepts and Andepts are directly associated with differences in pH and inversely related to organic C and CEC. Evidently the effects of organic C and CEC were small in comparison to the effects of pH.

TAB. 2. — *Data for noncompetitive Cu and Cd sorbed by the Encinas and Osorno soils and pH at 0.5 and 24 hr of incubation.*

Soil	Amount Added	Amount Sorbed	pH 0.5 hr	pH 24 hr
	cmmol kg^{-1}			
		Copper		
Encinas	0.19	0.19	6.36	6.95
	0.38	0.38	6.43	6.93
	1.90	1.83	5.81	6.41
	3.67	3.27	5.56	5.74
	18.41	8.01	4.98	4.91
		Cadmium		
Encinas	0.19	0.17	6.73	6.81
	0.36	0.32	6.51	6.49
	1.73	1.22	6.42	6.65
	3.55	2.44	6.35	6.48
	18.42	6.35	6.21	6.32
		Copper		
Osorno	0.19	0.19	5.08	5.12
	0.38	0.36	4.86	5.07
	1.89	1.44	4.69	4.82
	3.67	2.16	4.48	4.66
	18.41	4.55	4.37	4.37
		Cadmium		
Osorno	0.19	0.11	5.17	5.15
	0.36	0.19	5.19	5.14
	1.73	0.49	5.13	5.07
	3.55	1.09	5.03	5.02
	18.42	1.89	4.91	4.93

The sorption of each cation by the two Xerocrepts and also by the two Andepts were nearly the same so that the Encinas and Osorno soils were selected for more detailed studies.

Table 2 presents data for the noncompetitive sorption of Cu

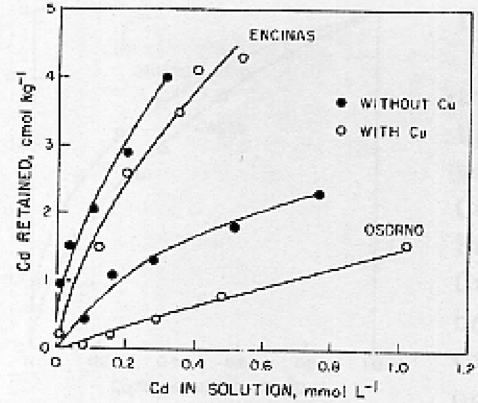

Fig. 1 — Relationship between Cd sorbed and Cd in solution with and without added Cu.

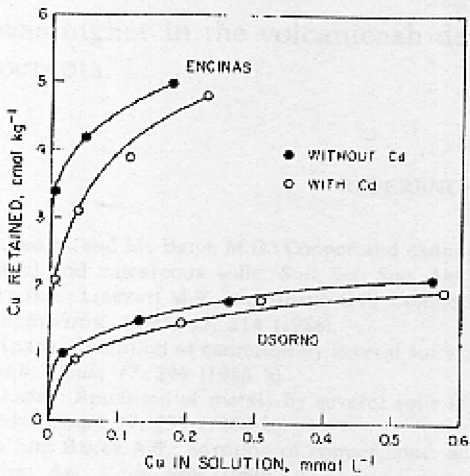

Fig. 2 — Relationship between Cu retained in the soil and Cu in solution with and without added Cd.

or Cd by the Encinas and Osorno soils and the pH of soil suspensions at 0.5 and 24 hr of incubation. For each soil the sorption of Cu was greater than that for Cd and for each cation the sorption was greater for the Encinas. Large decreases were measured in all cases but decreases were greater with Cu. There was a tendency for the pH to increase with increase in incubation time for the Encinas soil but this effect was inconsistent for the Osorno soil. pH values ranged from 4.91 to 6.95 and 6.21 to 6.81 for Cu and Cd, respectively, in the Encinas soil and from 4.37 to 5.12 and 4.91 to 5.19, respectively, for Cu and Cd in the Osorno soil.

The competitive sorptions of Cu and Cd are presented in Figs. 1 and 2. The addition of Cu had little effect on the reduction in Cd sorption in the Encinas soil but a large effect in the Osorno soil.

On the other hand, the addition of Cd had a larger effect on Cu sorption in the Encinas than in the Osorno. In the Osorno soil, Cu competed well against Cd but that Cd competed poorly againt Cu. In the Encinas soil, the competitive effect of Cu on Cd was about equal to the effect of Cd on Cu with a slight suggestion that the effect of Cd on Cu was greater than the effect of Cu on Cd. The pH values for the competitive effect of Cu on Cd or Cd on Cu ranged from 4.6 to 5.0 for the Osorno soil and 5.4 to 6.2 for the Encinas soil. The pH decreased with increase in

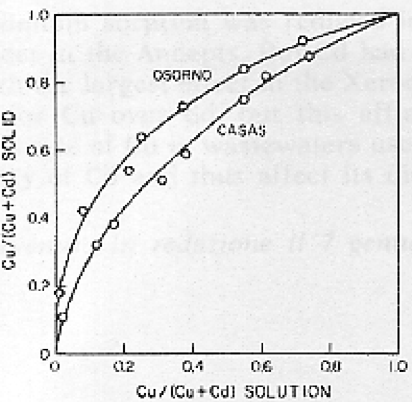

FIG. 3 — Relationship between mole fraction of the Cu sorbed and mole fraction of Cu in solution.

the sum of Cu plus Cd sorbed.

The relationships between the mole fraction of Cu sorption to mole fraction of Cu in solution for the Osorno and Casas soils are presented in Fig. 3. A large preference for Cu over Cd is indicated for both soils but was larger for the Osorno soil with its large organic C content. The relationships of Fig. 3 agree with those presented in Fig. 1 and 2, that Cu competition against Cd was higher in the volcanicash derived Osorno soil than in the Xerocrepts.

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SUMMARY. — Studies of Cd-Cu sorption by samples of two Andepts and two Xerocrepts indicated that for each soil the sorptions of both cations were nearly the same at low concentrations of less than 1.0 mmol L^{-1}. However, the sorption by Xerocrepts was about double that of the Andepts. This difference was related to pH but not to organic C or CEC.

Cadmium sorption was reduced in the presence of Cu with the largest effect in the Andepts. But Cd had a much smaller effect on Cu sorption with the largest effect in the Xerocrepts. All soils showed a higher affinity for Cu over Cd, but this affinity was highest in the Andepts. The presence of Cu in wastewaters used for irrigation could increase the mobility of Cd and thus affect its distribution throughout the soil profile.