Extraction by Barium Salts of Heavy Metals from Two Chilean Soils[1]

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ABSTRACT

Extraction of Cd, Cu, Ni, and Zn by $BaCl_2$ and $Ba(ClO_4)_2$ solutions from El Recuerdo (Vertisol) and Puerto Octay (Andept) soils was used to measure the amounts of metals remaining extractable during a 60-d storage period under air-dry and wet conditions. The El Recuerdo soil with an original pH of 7.3 sorbed about twice the amounts of metals sorbed by the Puerto Octay soil with an original pH of 5.5. The percent of the sorbed metal that remained extractable was in the order of Cd > Ni > Zn > Cu for El Recuerdo but Ni > Cd > Zn > Cu for the Puerto Octay soils. The decrease in pH associated with metal sorption was greatest for Cu which also showed the maximum fixation against extraction with Ba. The amounts of metals remaining extractable generally decreased with time, indicating that fixation reactions were essentially complete in 15 d in most cases and continued beyond the 15-d period in a few cases. The $BaCl_2$ solution desorbed more Cd than $Ba(ClO_4)_2$, but this effect of anion was not shown for the other metals, which agrees with the fact that the stability constants for soluble Cl complexes for Cd are greater than for the other metals. Only small and inconsistent differences were found for storage in air-dry as compared to wet conditions.

Additional Index Words: Vertisol, Andept, cadmium, copper, nickel, zinc, storage conditions, soluble chloride complexes.

A NUMBER of mechanisms are involved in the reactions of heavy metals with soils (Baker, 1980; Mortvedt et al., 1972; Page. 1974). Cation exchange with soil colloids, complex formation with organic matter, adsorption on surfaces of amorphous aluminosilicates and iron and aluminum oxides, and oxidation-reduction reactions can all play roles in metal reactions. Desorption or extraction of heavy metals, previously sorbed by soils, is one means of estimating the types of bonding that are involved (McLaren and Crawford, 1973; Silviera and Sommers, 1977; Stover et al., 1976; Schalscha et al., 1980). The exchangeable plus water-soluble fraction of metals can be extracted with salt solutions usually using the chloride or nitrate salts of K, Na, or Ba cations. However, the nature of the anion can introduce a variable as a result of the formation of soluble inorganic complexes with these anions (Benjamin and Leckie, 1979; Doner, 1978; Garcia-Miragaya and Page 1976; Hahne and Kroontje, 1973; Mattigod and Sposito, 1977). The use of perchlorate salts eliminates this variable in the extraction process because this ion does not form soluble complexes with metals.

The objectives of this research were to determine i) the amounts of metals sorbed and subsequently extracted by Ba salts, ii) the effects of time of storage in air-dry and wet conditions on extractable metals, and iii) the effect of anion on extractable metals. The metals studied were Cd, Cu, Ni, and Zn. The soils used were the El Recuerdo, a Vertisol, and the Puerto Octay, and Andept. The El Recuerdo soil is usually air dried before storage, whereas, it is common practice in Chile to store the Puerto Octay, and other volcanic-ash derived soils, in a wet condition to avoid changes in chemical properties that occur with drying. Also, the El Recuerdo soil had been irrigated with untreated sewage water for a period of 30 to 50 yr and had accumulated substantial quantities of metals. In contrast the Puerto Octay soil had never been irrigated and came from a site far from contamination by metals.

MATERIALS AND METHODS

Samples of the 5- to 30-cm depth of the El Recuerdo soil and of the 0- to 20-cm depth of the Puerto Octay soil were collected in May 1982. The El Recuerdo soil is a cultivated Vertisol (Torrert) derived from sediments of the Mapocho River, which originates in the Andes Mountains and traverses the city of Santiago. The dominant minerals are micas and montmorillonites. The sample collected had a saturated paste pH of 7.3, an organic C content of 20 mg g^{-1}, and a cation exchange capacity (CEC) of 0.30 mol $(Na^+)kg^{-1}$ at pH 7.0 as measured by the NaOAc method (Jackson, 1958).

The Puerto Octay soil, derived from volcanic ash in southern Chile, is an Andept (Dystrandept) characterized by high organic matter contents in the surface soil and mainly allophanic clays. The sample collected had a saturated paste pH of 5.5, an organic C content of 68.0 mg g^{-1}, and a CEC of 0.44 mol (Na^+) kg^{-1} at pH 7.0 as measured by the NaOAc method of Jackson (1958). The CEC of this soil is highly pH-dependent so that the CEC values at acid pH values are much lower than the value listed for the NaOAc method. The El Recuerdo and Puerto Octay soils are identified as ER and PO, respectively, in the remainder of the paper.

The ER soil was air dried whereas the PO soil was kept at its field water content. Water contents were determined by drying at 105° for 24 h. To prepare soil materials for extraction of metals, 20-g samples of soil were equilibrated for 24 h with 400 mL of metal perchlorate solutions at concentrations of 5.0×10^{-4} and 5.0×10^{-3} M. After shaking for 24 h, the suspension was centrifuged and the pH was determined in the supernatant. The soil was then washed twice with 100 mL of redistilled water. The metal not recovered in the supernatant and in the washings was designated as that sorbed.

Extraction of metals was accomplished by shaking 20 mL of 0.10 M $BaCl_2$ or $Ba(ClO_4)_2$ solution with soil samples representing 1 g of dry matter for 24 h followed by centrifugation and the determination of the metal concentration in the supernatant. The pH of the Ba solutions was 5.2, but because these solutions are poorly buffered and the soils are highly buffered, the soils controlled the pH of the extraction process. To determine the effects of time of storage on extraction of metal, samples equivalent to 2 g of dry soil were stored for 15, 30, and 60 d in air-dry and water-saturated conditions, after which the metals were extracted with Ba salts using the procedure as described. The samples were stored in 50-mL centrifuge tubes. The air-dry samples were left uncovered and allowed to equilibrate with the water

Table 1—Amounts of metals sorbed and extracted by $0.1M$ Ba(ClO$_4$)$_2$ and pH values of supernatant solutions during sorption and during extraction.

Metal	Amount sorbed[†]	pH during sorption	Amount extracted	% extracted	pH during extraction[‡]	Amount fixed
	mmol kg^{-1}		mmol kg^{-1}			mmol kg^{-1}
			El Recuerdo soil			
Cd	7.6	7.4	4.7	61.8	7.0	2.9
	65.0	6.5	52.1	80.2	6.3	12.9
Cu	9.7	7.1	0.1	0.1	6.7	9.6
	82.9	4.8	38.3	46.2	5.2	44.6
Ni	8.7	7.4	4.4	50.6	6.7	4.3
	56.1	6.7	43.1	76.8	6.4	13.0
Zn	9.2	7.4	1.6	17.4	6.9	7.6
	64.3	6.4	42.6	66.3	6.7	21.8
			Puerto Octay soil			
Cd	4.9	5.3	4.6	93.9	4.7	0.3
	35.8	4.7	17.7	49.4	4.8	18.1
Cu	9.8	4.8	2.2	22.4	4.7	7.6
	41.5	4.4	13.9	33.5	4.7	27.6
Ni	5.4	5.4	5.2	96.3	4.7	0.2
	17.8	5.0	15.5	87.1	4.8	2.3
Zn	3.6	5.4	2.8	77.8	4.7	0.8
	32.6	5.0	15.4	47.2	4.7	17.2

† Lower and higher amounts sorbed in all metal-soil combinations were from initial concentrations of 5.0×10^{-4} and 5.0×10^{-1} M perchlorate salts, respectively.

‡ pH of the supernatant solution following a 24-h period of shaking of soil samples in suspension in metal perchlorate or Ba(ClO$_4$)$_2$ solutions.

Table 2—Metals extracted by $0.1M$ BaCl$_2$ and Ba(ClO$_4$)$_2$ solutions.

Metal	Amount sorbed	Extracted metal BaCl$_2$	Ba(ClO$_4$)$_2$	Level of significance[†]
	mmol kg^{-1}	— % of amount sorbed —		
		El Recuerdo soil		
Cd	7.6	86.8	50.8	***
	65.0	90.1	77.8	***
Cu	9.7	1.51	1.12	NS
	82.9	41.6	39.4	NS
Ni	8.7	55.3	53.9	NS
	56.1	68.1	69.8	NS
Zn	9.2	17.8	17.4	NS
	64.3	59.2	57.2	NS
		Puerto Octay soil		
Cd	4.9	93.8	81.1	**
	35.8	44.8	40.2	NS
Cu	9.8	13.8	15.0	NS
	41.5	24.0	29.3	***
Ni	5.4	91.9	90.5	NS
	17.8	76.3	77.3	NS
Zn	3.6	64.6	69.6	NS
	32.5	32.5	34.3	NS

† NS indicates nonsignificance at the 5% level and *, **, and *** indicate significance at the 5, 1, and 0.1% levels, respectively.

vapor of the laboratory air. The wet samples were covered with a small amount of redistilled water and then stoppered with no special precautions to avoid air exchange. The amount of O$_2$ in the water and air in the centrifuge tube was considered sufficient to prevent anaerobiosis.

All data presented represent the means of at least duplicate samples for the determination of extracted metals. The relative deviations of duplicate values were < 6%.

RESULTS

Data for amounts of metals sorbed from solutions of metal perchlorates, amounts extracted by $0.1M$ Ba(ClO$_4$)$_2$ solution immediately following the sorption and washing processes, and the amounts of metals fixed against extraction with Ba(ClO$_4$)$_2$ are presented in Table 1. Also presented are pH values of supernatant solutions during the sorption and extraction processes. Ratios of metals sorbed by the ER soil to those sorbed by the PO soil were 1.8, 2.0, 3.2, and 2.0, respectively, for Cd, Cu, Ni, and Zn at the higher level of sorbed metals and 1.6, 1.0, 1.6, and 2.6, respectively, for the lower levels.

For both levels of sorbed metals in the ER soil, the amounts extracted and the percent extracted were in the order of Cd > Ni > Zn > Cu. For the PO soil, the percent extracted was in the order of Ni > Cd > Zn > Cu for both levels of sorbed metals. The amount extracted was in the order of Ni > Cd > Zn > Cu for the lower level, but Cd > Ni > Zn > Cu for the higher level.

The amounts of metals fixed against extraction with Ba(ClO$_4$)$_2$ was in the order of Cu > Zn > Ni > Cd for both levels of sorbed metals in the ER soil. This was the exact reverse order of extractability for metals in this soil. However, for the PO soil the order was Cu > Zn Cd > Ni at the lower level of sorbed metals

and Cu > Cd > Zn > Ni at the higher level. These are not in the reverse order as those for the extractability expressed in percent of amounts sorbed. At the lower amounts of sorbed metals, the amounts of Ni and Cd fixed are small and the difference between these two metals is small and is likely the result of analytical errors. However, at the higher levels of sorbed metals the amount of Cd fixed in the PO soil at pH 4.7 was greater than in the ER soil, whereas the Ni fixed in the PO soil at pH 5.0 was 18% of that fixed by the ER soil at pH 6.7. Evidently there is a mechanism of precipitation or specific sorption of Cd in the PO soil that is not functioning for Ni. This difference in reactivity of the PO soil for Cd, as compared to Ni, could be a result of its high organic matter or high allophane contents. Both soils have reactive organic matter, but only the PO soil has allophane in any measurable amount. Thus, this higher fixation of Cd is likely a function of allophane, rather than organic matter.

The data for the metal extracted for each treatment of each soil were subjected to an analysis of variance to test the statistical significance of effects of storage time, storage condition, and the anion in the extracting solution. Because replication was not available, separate analyses were performed for each variable using the data for other variables as replications. For example, the effect of the anion was tested using the data for the effects of storage time and storage condition as replications.

The data for metals extracted by $0.1M$ BaCl$_2$ and Ba(ClO$_4$)$_2$ solutions are presented in Table 2. The data are averages for 0-, 15-, 30-, and 60-d storage periods and for air-dry and wet conditions. The Ba(ClO$_4$)$_2$ solution extracted significantly more Cd from both Cd treatments of the ER soil and from the lower level of sorbed Cd on the PO soil. For the higher level of sorbed Cd (PO soil), BaCl$_2$ extracted more than Ba(ClO$_4$)$_2$ but the difference was not significant statistically. The only other statistically significant difference was for the high

Table 3—Effects of air-dry vs. wet conditions during storage
on metals extracted.

Metal	Amount sorbed	Metal extracted		Level of significance†
		Air-dry condition	Wet condition	
	mmol kg⁻¹	— % of amount sorbed —		
		El Recuerdo soil		
Cd	7.6	67.4	68.4	NS
	65.0	84.9	81.4	NS
Cu	9.7	0.87	1.89	*
	82.9	36.5	42.8	*
Ni	8.7	56.0	54.0	NS
	56.1	69.5	63.3	*
Zn	9.2	16.0	16.4	NS
	64.3	57.2	52.7	*
		Puerto Octay soil		
Cd	4.9	76.6	89.5	**
	35.8	45.5	33.7	**
Cu	9.8	10.4	14.5	**
	41.5	25.6	23.3	NS
Ni	5.4	90.4	88.3	NS
	17.8	81.3	66.3	***
Zn	3.6	61.7	63.6	NS
	32.5	32.4	25.6	**

† NS, *, **, and *** indicate nonsignificant, and significant at the 5, 1, and
0.1% levels, respectively.

Table 4—The effect of time of storage on metals extracted.

Metal	Amount sorbed	Metal extracted at			
		0 d	15 d	30 d	60 d
	mmol kg⁻¹	— — — — % of amount sorbed — — —			
		El Recuerdo soil			
Cd	7.6	76.6 a*	71.7 a	64.6 ab	61.8 b
	65.0	86.2 a	84.3 ab	83.7 ab	81.4 b
Cu	9.7	1.12 a	1.86 a	1.17 a	1.12 a
	82.9	48.4 a	41.3 b	37.4 bc	34.8 c
Ni	8.7	53.4 ab	61.0 a	57.8 a	46.3 b
	56.1	76.4 a	68.3 b	68.8 ab	62.2 b
Zn	9.2	21.8 a	19.0 ab	15.0 b	14.7 b
	64.3	67.9 a	54.6 b	54.9 b	55.4 b
		Puerto Octay soil			
Cd	4.9	101.0 a	85.2 b	82.6 b	81.1 b
	35.8	52.1 a	39.9 b	39.6 b	39.3 b
Cu	9.8	20.4 a	11.4 b	13.1 b	12.8 b
	41.5	32.7 a	23.0 c	26.1 b	24.9 bc
Ni	5.4	96.8 a	87.1 a	95.4 a	85.6 a
	17.8	86.0 a	72.6 b	74.3 b	74.4 b
Zn	3.6	80.6 a	67.4 b	62.1 c	58.4 d
	32.6	46.6 a	31.3 b	28.7 b	27.0 b

* Values within each line not followed by the same letter are significantly
different at the 5% probability level by the Duncan's multiple range test.

level of Cu sorbed on the PO soil, but, in this case,
$Ba(ClO_4)_2$ extracted the greater amount. Thus, the only
consistent effect of the anion was with Cd.

Data for the extracted metals for air-dry and wet
storage conditions are presented in Table 3. In this
case, the data are means for three incubation periods
and for both extracting solutions. Significant differ-
ences were found in four treatments of the ER and
five treatments of the PO soils. In four of these nine
treatments the amounts of metal extracted were greater
for the wet storage indicating that the reactions that
fixed metals against extraction with Ba salts were
greater in the air-dry than in the wet samples. How-
ever, six cases of significance were for the higher level
of sorbed metals, and, in five of these cases, the ex-
tracted metals were greater for the air-dry storage. The
exception was for Cu. In the three cases of significance
for the lower level of sorbed metals, more metals were
extracted from the samples that were stored in a wet
condition.

There were no visible evidences of reducing con-
ditions in the samples stored under wet conditions.
Also, the pH values of the supernatant liquid follow-
ing extraction of the wet samples ranged from 5.3 to
6.9 for the ER soil and 4.7 to 4.9 for the PO soil as
compared to pH values near 7 that would have de-
veloped if anaerobic conditions had existed (Ponnam-
peruma, 1972). The pH values of the supernatant dur-
ing extractions were nearly the same for air-dry and
wet samples, with differences of 0.1 pH units or less
for nearly all comparisons. Also, pH values did not
change with time of storage.

Data for metals extracted by Ba salts at 0-, 15-,
30-, and 60-d storage periods are presented in Table
4. The data represent means of two extracting solu-
tions and two storage conditions. Except for the low
level of sorbed Cu for the ER soil and the low level
of sorbed Ni in the PO soil, the extracted metals de-
creased with increasing time of storage. In most treat-

ment-soil combinations, however, the decreases in ex-
tracted metals occurred during the first 15 d of storage
with only small and mostly nonsignificant decreases
with increasing storage time. Only in the cases of the
higher level of sorbed Cu in the ER soil and the lower
level of sorbed Zn in the PO soil were there consistent
reductions in extracted metals with increase in time
up to 60 d of storage.

DISCUSSION

The large differences in amounts of metals sorbed
by the ER and PO soils are associated with large dif-
ferences in pH values, and could be related to differ-
ences in effective CEC, which are also associated with
pH. The differences in metals sorbed could also be
related to differences in types of clays and the amounts
and reactivities of organic matter. Except for the Cu
treatment of the ER soil, the pH values during the
reaction with the higher metal perchlorate concentra-
tion ranged from 6.4 to 7.1, inclusive, for the ER soil
and 4.4 to 5.0, inclusive, for the PO soil.

The CECs of both soils are pH dependent. Using a
CEC-pH curve for the PO soil developed by Thomas
(1969) and a calculated CEC-pH curve for the ER soil,
approximate CEC values were estimated for each re-
action pH for metal treatments using the higher metal
perchlorate concentration. For the ER soil, the CEC-
pH curve was calculated from the determined value
of 300 mmol $(+)$ kg⁻¹ at pH 7 and the slopes of such
curves for several Californian soils dominated by
montmorillonite and micaceous clays having organic
C contents similar to that of the ER soil (Pratt and
Bair, 1962).

Data for estimated CEC values for reaction pH val-
ues and for metals extracted, expressed as percent of
the effective CEC values, are presented in Table 5. If
CEC were the dominant factor in metal behavior in
these two soils, the metals extracted (expressed as per-
cent of the CEC) would have been nearly the same in
both soils. Actually, the ER soil retained extractable

Table 5—Estimated CEC values at the pH during sorption and for metals extracted by Ba(ClO₄)₂ from ER and PO soils treated with the higher metal perchlorate solution concentration.

Metal	pH ER	pH PO	CEC at pH of sorption reaction ER	CEC at pH of sorption reaction PO	Metal extracted ER	Metal extracted PO
			mmol(M⁺⁺) kg⁻¹		% of CEC	
Cd	6.5	4.7	133	82	39.2	21.6
Cu	4.8	4.4	103	55	37.2	18.3
Ni	6.7	5.0	140	89	30.8	17.4
Zn	6.4	5.0	130	89	32.6	17.2

Table 6—Stability constants (log K) for Chloro complexes of Cd, Cu, Ni, and Zn.†

Chloro species	Cd	Cu	Ni	Zn
	log K			
MCl^-	1.98	0.40	0.72	0.43
MCl_2^0	2.60	0.16	0.70	0.18

† Taken from Smith and Martell (1976).

few days of storage. In the case of air-dry storage, these reactions could have occurred during the drying process.

metals equal to 1.8 to 2.0 times the retention in the PO soil when expressed as percent of the CEC. When actual amounts of metals extracted are compared, the ratios for the ER to PO soils are 2.8 to 2.9. This indicates that the effective CEC values explain some of the differences between the two soils. But other factors are involved. One of these might be the reactivity of the organic matter. The PO soil was more than 3 times more organic C, but the organic matter in this soil is noted for its great stability.

For each metal adsorbed by the ER soil, the percent that remained exchangeable or extractable by Ba salts increased with increasing amount sorbed. A partial explanation for this behavior is that the pH at the higher amount sorbed was lower, in agreement with the well known effect of pH on reactions of metals with soils (Bar-Yosef, 1979; Kuo and Baker, 1980; McBride and Blasiak, 1979; Adams et al., 1982). However, in the PO soil, the percent that remained extractable decreased with increasing amounts sorbed for Cd, Ni, and Zn, but not for Cu. The pH values for this soil during extraction with Ba(ClO₄)₂ ranged from 4.7 to 4.8. With such a limited pH range, the pH effect would be small and the usual phenomenon of decreased percent fixation with increasing amount added was evidently dominant for Cd, Ni, and Zn, but not for Cu.

The effect of BaCl₂, as compared to Ba(ClO₄)₂, extraction should be related to the formation of soluble complexes with Cl⁻. The ClO₄⁻ anion is considered to form no soluble metal complexes, whereas Cl⁻ forms MCl^+ and MCl_2^0 complexes. The stability constants for Cd, Cu, Ni, and Zn (Table 6) suggest that sufficient $CdCl_2^0$ might form to increase desorption of Cd in BaCl₂ as compared to Ba(ClO₄)₂. These stability constants explain why Cd was the only metal for which there was a consistently greater amount extracted by BaCl₂.

The effect of storage condition was inconsistent and most differences were small. One could conclude that for the reactions of metals with Vertisols and Andepts, there are no advantages to either storage conditions, and that air drying before storage has no disadvantages. The reactions that increased the fixation of metals against extraction with Ba seem to have occurred largely during the first 15 d of storage. Judging from the shapes of extracted metals vs. time curves, most of these reactions could have occurred during the first

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