

Chemical Indices of Soil Quality: Effects of Heavy Metal Additions

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The objective of this research was to characterize effects of Cu or Cd additions on chemistry of soil quality indices, such as pH, EC, cation distribution and buffering capacity. Metals were added at rates ranging from 0 to 400 mg·kg⁻¹ of soil. Soil solution was sequentially extracted from saturated pastes using vacuum. Concentrations of Cu or Cd remaining in soil solutions were very low as compared to those added to the soils, warranting that most of the added metals were recovered as nonavailable fractions. Adsorption of the added metals released cations into soil solution causing increases of ionic strength of soil solution. At metal additions of 200~400 mg·kg⁻¹, EC of soil solution increased to as much as 2~4 dS·m⁻¹; salinity levels considered high enough to cause detrimental effects on plant production. More divalent cations than monovalent cations were exchanged by Cu or Cd adsorption. The nutrient buffering capacity of soils was decreased due to the metal adsorption and release of cations. pH of soil solution decreased linearly with increasing metal loading rates, with a decrement of up to 1.3 units at 400 mg Cu·kg⁻¹ addition. Influences of Cu on each of these soil quality parameters were consistently greater than those of Cd. These effects were of a detrimental nature and large enough in most cases to significantly impact soil productivity. It is clear that new protocols are needed for evaluating potential effects of heavy metal loading of soils.

Key words : heavy metal, soil chemical quality, soil solution, fractionation, buffering capacity.

Soil accumulations of some heavy metals continue to increase due to inputs from a variety of point and non-point sources. Heavy metal contamination may cause toxicity to plants and other soil biota, as well as creating an avenue for metal entrance into the human food chain.¹⁻³⁾ To date, no simple, uniform protocols have been developed for assessing heavy metal impacts on soils. Current assessment is based on measurement of total contents or metal extractability using specific chemicals.³⁻⁵⁾ Although these values may serve as indices for pollution, they do not describe metal bioavailability, biotoxicity, transport, or fate in the soil. These processes are regulated by specific physicochemical forms (chemical species) and their soil reactions, rather than total or extractable concentrations.^{4,6-8)} Methodologies showing promise to better evaluate soil contamination effects include chemical speciation, frac-

tionation, direct determination of plant-uptake relations, and modeling.^{6,9-11)}

Metals are generally most toxic in their ionic forms.^{4,7,8,12)} Metal ion concentrations in soil, however, are usually very low because these ions are adsorbed strongly onto soil colloids, or they form complexes with organic and inorganic ligands in the soil solution.^{6,8,13-15)} Products formed by these reactions have high stability constants, resulting in limited metal bioavailability and toxicity. Other than direct toxicity, however, heavy metals may alter the balance of soil chemical and biological reactions, causing indirect or secondary influences on soil quality.

Awareness of soil as a critical component of the earth biosphere has stimulated interests in evaluating the quality of soils as they are subjected to various management regimes. Doran and Parkin¹⁶⁾ defined soil quality as the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health. Adequate assessment of soil quality must include consideration of the soil as a multi-functional body involving physical, chemical and biological processes. Important chemical indicators of soil function include a variety of nutrient

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Abbreviations: AAS, atomic absorption spectrophotometer; BC, buffering capacity; CC, chemical concentrations; DTPA-TEA, diethylenetriaminepentaacetic acid-triethanol amine; EC, electrical conductivity.

availability parameters, such as pH, cation exchange capacity, EC, and nutrient contents and their distribution in solid and liquid phases. Few studies have been reported to characterize heavy metal effects on these soil properties and how they may alter biological productivity. Objective of this research was to investigate how Cu or Cd contamination of soils may change basic soil chemistry indices that relate to soil quality and productivity.

Materials and Methods

Soil samples. Soil samples were collected from 0–30 cm depth of three upland fields where metal contaminants had never knowingly been introduced. Extraction by DTPA-TEA¹⁷ supported evaluation of these as non-contaminated soils (Table 1). Samples were air dried, ground, and sieved to 2 mm. Selected chemical properties of the experimental soils are shown in Table 1.

Soil solution extraction. Subsamples (150 g) were contaminated with Cu or Cd by adding predetermined amounts of Cu or Cd solutions, as chloride salts, to make saturated pastes. Concentrations of Cu or Cd ranged from 0 to 400 mg·kg⁻¹ soil. Pastes were made in 250 ml screw-cap polyethylene extraction cups and equilibrated at 25°C for 24 h. After 24 h, each saturated paste was filtered using vacuum pump on a Buchner funnel fitted with Whatman No. 42 filter paper. Extracted solutions were re-filtered through a 0.45 µm membrane filter paper, and their volume, pH, and EC were immediately measured. Solutions were stored at 4°C for further analyses for soluble cations (K, Na, Ca and Mg) and heavy metals (Cu and Cd) by AAS. Extracted soils were re-saturated by adding an aliquot of water equivalent to the volume of soil solution extracted. These pastes were re-equilibrated at 25°C for 24 h and the same process was repeated as described above until five cycles had been completed. At each cycle, about 5 g of soil subsamples were taken to analyze exchangeable (1 M NH₄OAc, pH 7.0) cations (K, Na, Ca and Mg) and DTPA-TEA extractable Cu or Cd¹⁷ by AAS. Each experimental treatment was replicated four times.

Fractionation of heavy metals. A separate sample of silt loam soil was added with 100 mg (Cu or Cd)·kg⁻¹, using the saturated paste method described above, and equilibrated at 25°C for 5 days. The soil paste was air-dried and sequentially extracted by the method of Keller

and Vedy⁹) to determine water soluble, exchangeable, Mn-oxide bound, Fe-oxide bound, organically bound, and residual fractions.

Soil chemical quality indices. The regression model (eq. 1) was used to evaluate changes of soil chemical quality parameters (ΔCP) in the solution phase over the five-extraction series as a function of heavy metal concentration ($[C]_{hm}$).

$$\Delta CP = f\{[C]_{hm}\} \quad (1)$$

Changes in soil buffer capacity (BC) from addition of heavy metals were evaluated, using eq. 2, from the relationship between exchangeable cations (ΔQ) and those cations in soil solution (ΔI).

$$BC = \Delta Q / \Delta I \quad (2)$$

Changes in buffer capacity (ΔBC) were curve-fitted to heavy metal concentrations ($[C]$) as eq. (3)

$$BC = a + b \log[C] \quad (3)$$

From these models, CC_{Xn} of Cu or Cd required to change each soil-quality related chemical parameter (X) by a selected amount (n) were assessed.

Results

Heavy metals in soil solution. Concentrations of Cu or Cd remaining in the soil solution were very low as compared to those added to each of the three soils, indicating that most of these metals were adsorbed onto the solid phase (Table 2). Metal concentrations did, however, increase by increasing rate of metal addition. Less Cu than Cd remained in solution at equal rates of addition, indicating higher specificity of soils for adsorbing Cu, corresponding to previous reports.¹³⁻¹⁵ No Cu was detected in soil solutions where the rate of application was less than 80 mg Cu·kg⁻¹, and only 0.4 to 5% of added Cu quantities at rates above 200 mg·kg⁻¹ were recovered in soil solution. As much as 26% of Cd added at the highest rates was present in soil solution. Based on earlier reports, it is probable that the forms of Cu and Cd in soil solution were free ions.^{6,11}

Less Cu or Cd remained in solution with the coarser SL soil than in the finer textured C and SiL soils (Table 2). This is probably due to the higher organic matter content of the SL soil, which was about 1½ and 2 times

Table 1. Physical and chemical properties of the experimental soils.

Soil Texture	pH	Organic Matter	CEC	Exchangeable Cations				DTPA-Cu	DTPA-Cd
				K	Ca	Mg	Na		
	(1:5)	g·kg ⁻¹	cmol(+)·kg ⁻¹	----- cmol(+)·kg ⁻¹ -----				mg·kg ⁻¹	mg·kg ⁻¹
SL	7.68	33.4	7.3	0.93	3.92	2.23	0.21	0.16	0.03
SiL	5.45	20.1	8.5	0.14	3.18	0.58	0.10	0.36	0.03
C	6.32	13.6	11.8	1.71	3.97	1.16	0.14	0.93	0.07

Table 2. Relative percentages of Cu or Cd remaining in soil solution as compared to the amounts of metals treated in three textural soils.

treatment	Cu				Cd			
	Treatment	SL	SiL	C	Treatment	SL	SiL	C
mg · kg ⁻¹	mmole · kg ⁻¹	----- % -----			mmole · kg ⁻¹	----- % -----		
0	0.00	ND ^a	ND ^a	ND ^a	0.00	ND ^a	ND ^a	ND ^a
10	0.16	ND ^a	ND ^a	ND ^a	0.09	ND ^a	ND ^a	1.10
20	0.32	ND ^a	ND ^a	ND ^a	0.18	ND ^a	1.45	1.15
40	0.63	ND ^a	ND ^a	ND ^a	0.36	0.03	2.55	1.43
80	1.26	ND ^a	ND ^a	0.50	0.71	0.10	3.88	1.44
100	1.57	0.29	ND ^a	0.58	0.89	0.20	4.53	4.47
200	3.15	0.39	0.57	1.83	1.78	0.49	11.42	12.21
400	6.30	1.41	3.10	5.22	3.56	1.42	27.20	25.88

^aNot Detectable.

higher than that of SiL and C soil, respectively. It is well known that organic colloids in soils have particularly strong affinity for Cu.^{15,18)}

Adsorbed fractions of metals. Results of metal fractionation on the SiL soil treated with 100 mg · kg⁻¹ of Cu or Cd are presented in Table 3. This fractionation scheme sequentially extracts adsorbed fractions, first using water, followed by weak solutions, more acidic extractants, and finally organic-decomposing chemicals.⁹⁾ Water soluble and exchangeable (NaNO₃-extractable) fractions of Cu were not detectable. These are the forms considered available for plant uptake, suggesting that little or no Cu, when added to soils at this rate, would be bioavailable. Most (86%) of the added Cu was oxide- and organically-bound. Under current standards, soil having a total concentration of 100 mg Cu · kg⁻¹ (regardless of forms) would be considered contaminated, even though little of this Cu would be bioavailable. This illustrates the need to develop protocols to assess effects of heavy metals in soils, based on availability concepts.

Only about 11% of adsorbed forms of Cd were water soluble and exchangeable (available), with most of it being oxide-bound. Less than 10% of Cd was tied up by organic matter as compared to Cu. Hickey and Kittrick¹⁹⁾ reported similar results, showing that Cu was the only metal significantly associated with the organic fraction. Rule and Alden III²⁰⁾ reported that Cu and Cd in estuarine sediments were mostly organic-sulfide, acid extractable, and easily reducible fractions, with very small exchangeable

fractions. Bioavailability and mobility of these metals are directly related to quantities of their ionic (available) forms in the soil. Hence, these results further support the concept that Cd is more mobile, and potentially more toxic, than Cu. Different loading rates for these metals are probably warranted for soil management directives.

Changes of soil solution pH. Fig. 1 presents effects of Cu or Cd rates on saturated paste extract pH in each soil. All pHs decreased in proportion to rate of Cu or Cd addition, due to proton release from soil colloids as more Cu or Cd were adsorbed. In each soil, the pH decrement was greater from Cu than from Cd. This corresponds to the above results that indicated more adsorption of Cu than Cd. At 400 mg Cu · kg⁻¹ treatment, solution pHs decreased 0.55, 0.93 and 1.26 units in the SL, SiL and C soils, respectively. The greater apparent pH buffer capacity of the coarser textured soil was probably related to differences in organic matter content and degree of base saturation (Table 1).

Linear models between pH and Cu or Cd treatment for each soil are presented in Table 4, illustrating a highly significant linear relationship. Based on this, we calculated from Table 4 models the chemical concentrations of metal application required to decrease pH by 0.5 units ($CC_{pH0.5}$). These values ranged from 118.8 to 351.7 mg · kg⁻¹ for Cu and from 95.2 to 530.6 mg · kg⁻¹ for Cd. We did not find similar reports for comparison, but these results suggest that soils may be reasonably well buffered against pH changes unless rather high rates of Cu, and even higher

Table 3. Fractionations^a of adsorbed Cu or Cd in SiL soil when metals were added at 100 mg · kg⁻¹.

Fractions	Extractants	Cu		Cd	
		%	Cum % ^b	%	Cum % ^b
Water soluble	Water	0.00	0.00	0.70	0.70
Exchangeable	0.01 M NaNO ₃	0.00	0.00	10.68	11.38
Mn Oxide bound	0.1 M NH ₂ OH-HCl	11.26	11.26	64.79	76.17
Fe Oxide bound	1 M NH ₂ OH-HCl	45.75	57.01	19.51	95.68
Organically bound	H ₂ O ₂ (30%)+0.02M HNO ₃	29.20	86.21	2.79	98.47
Residual	Aqua Regia	13.80	100.00	1.54	100.00

^aFractionation scheme was followed by the method of Keller and Vedy (1994).

^bCumulative percentages.

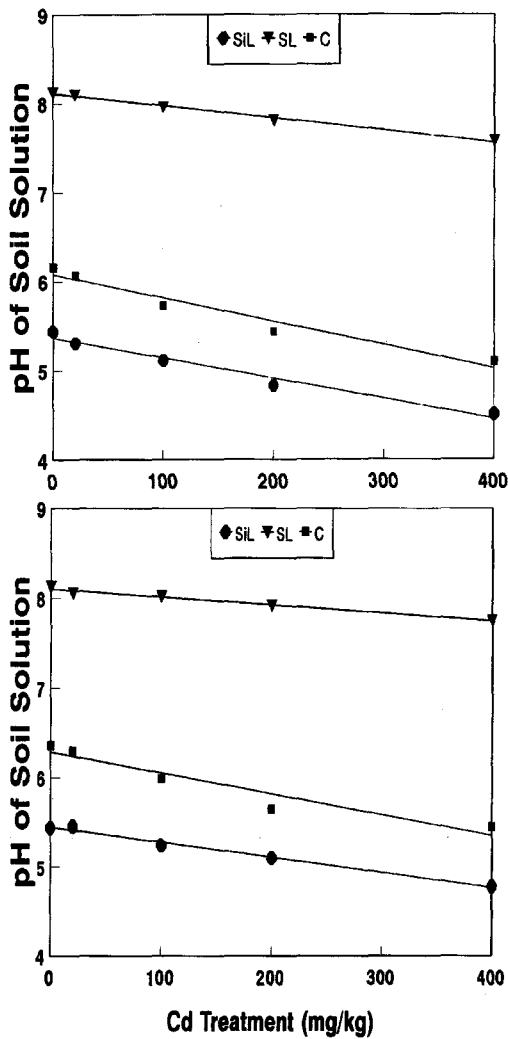


Fig. 1. Influences of Cu or Cd treatments on pH of the soil solution in three soils.

Table 4. Relationships between pH of soil solution (Y) and metal rate (X), and chemical concentration of Cu or Cd required to decrease pH 0.5 unit ($CC_{pH0.5}$).

Soils	Metals	Regression Models	r	$CC_{pH0.5}$ mg · kg ⁻¹
SL	Cu	$Y=8.11-1.42 \times 10^{-3} X$	-0.996***	351.7
	Cd	$Y=8.12-0.94 \times 10^{-3} X$	-0.992***	530.6
SiL	Cu	$Y=5.38-3.11 \times 10^{-3} X$	-0.994***	160.5
	Cd	$Y=5.45-1.67 \times 10^{-3} X$	-0.993***	299.1
C	Cu	$Y=6.13-5.25 \times 10^{-3} X$	-0.963***	118.8
	Cd	$Y=6.31-4.21 \times 10^{-3} X$	-0.965***	95.2

***: Significant at $p < 0.01$.

rates of Cd, are added. This approach merits attention as a tool for soil contamination assessment.

Changes of cation distribution in soil solution. The mass (μmol) of each cation in solution (K, Ca, Mg and Na) from the SL soil (bar graphs) and summations of cations in all three soils (lines), as affected by Cu or Cd treatments, are presented in Fig. 2. Each soluble cation content increased with increased rate of metal addition, illustrating the effects of metal salts on the process of

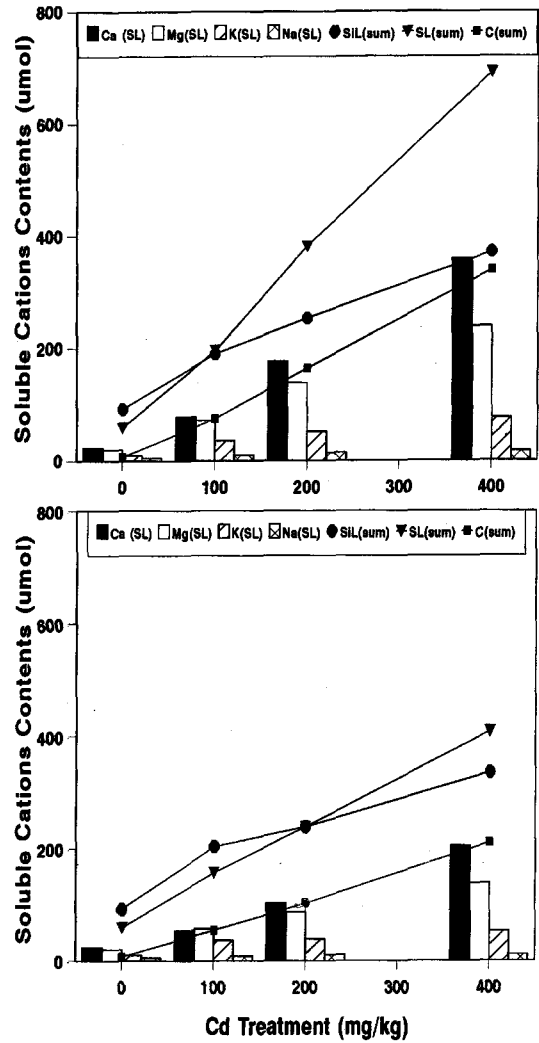


Fig. 2. Contents of Ca, Mg, K and Na in soil solution (μmol) of SL soil (bars), and the summations of these cations in three soils (lines).

cation exchange. Results were similar for all three soils. More cations were exchanged by Cu than by Cd at the same level of treatment, and more divalent than monovalent cations were exchanged. The stoichiometric order of exchange was $\text{Ca} \geq \text{Mg} > \text{K} > \text{Na}$ in all three soils.

Fig. 3 shows the changes of relative distributions of each cation as compared to total cations in soil solutions. Higher Cu or Cd additions increased relative contents of divalent cations (Ca+Mg) in solution, but those of monovalent cations (K+Na) decreased. It is clear that, as divalent Cu or Cd were adsorbed on soil particles, they replaced mostly other divalent ions. Slight differences were observed between amounts of Ca and Mg, or K and Na.

Fig. 4 shows the effects of heavy metal treatments on total cations (Ca+Mg+K+Na) in solution at each sequential extraction of soil solution in the SL soil. As the number of extractions increased, total cation contents (μmol) in solutions significantly decreased, with the greatest decrease

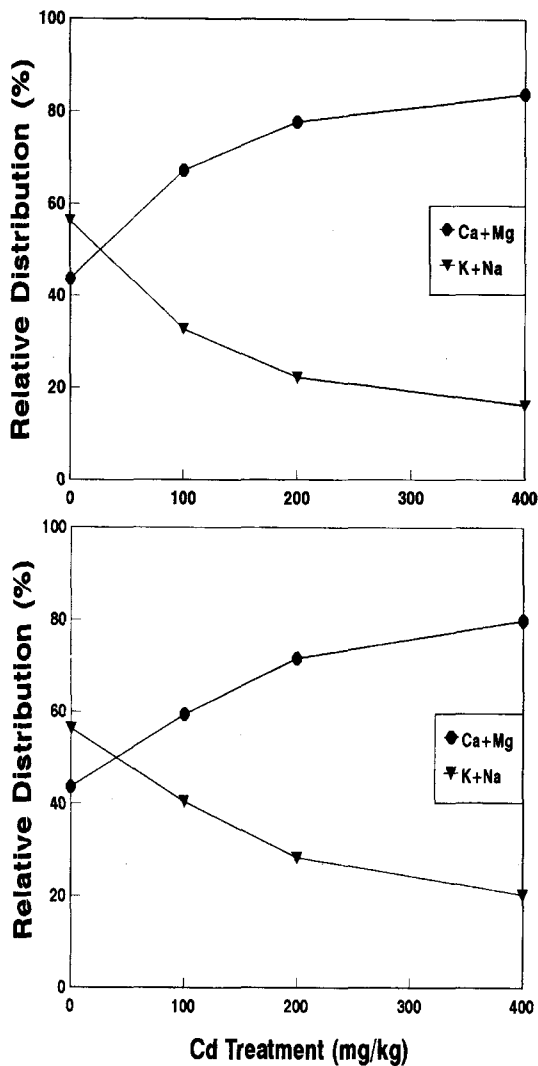


Fig. 3. Relative distribution (%) of divalent (Ca and Mg) and monovalent (K and Na) cations in soil solutions of SL soil as influenced by Cu or Cd treatments.

occurring after the third extraction.

Plants absorb cations mostly as ions from the soil solution.¹⁸⁾ Thus, our results suggest that additions of heavy metals may initially increase cation nutrient availability, but subsequently their availability would decrease. Considering that most heavy metals in soils are strongly adsorbed and immobile, assessment of soil chemical parameters that influence nutrient availability may be an appropriate approach to evaluate contamination consequences. Considering only potential toxicity may be misleading when evaluating long-term effects.

Changes of electrical conductivity in soil solution.

The ECs of soil solution increased in all soils in direct relation to rate of Cu or Cd addition (Fig. 5). Again, Cu had a greater effect than did Cd. The increased ECs can be attributed to increased cations in soil solution, along with associated anions required to maintain electrical neutrality. Thus, even though the effect on EC is not due to soluble Cu or Cd, the indirect effect of their addition

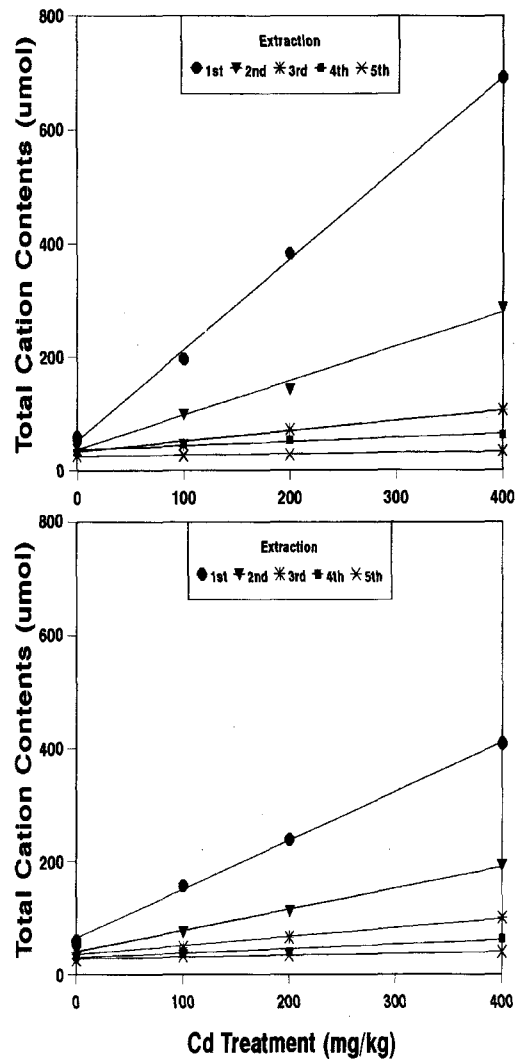


Fig. 4. Total soluble cation contents (Ca+Mg+K+Na; μmol) in each soil solution of five sequential extractions in SL soil.

can be evaluated.

Soil salinity, as evaluated based on EC of saturated pastes,²¹⁾ may potentially influence the yield of very sensitive crops at a level of $2 \text{ mS}\cdot\text{cm}^{-1}$. If electrical conductivity is $4 \text{ mS}\cdot\text{cm}^{-1}$ or more, yields of many crops are restricted. Readings in the 2 to $4 \text{ mS}\cdot\text{cm}^{-1}$ range were recorded for the SiL and SL soils at Cu addition of $>200 \text{ mg}\cdot\text{kg}^{-1}$ and at $400 \text{ mg}\cdot\text{Cd}\cdot\text{kg}^{-1}$. These elevated salinity levels would likely have detrimental effects on most crops, even if metal toxicity was not a problem.

From data in Fig. 5, rates of Cu or Cd addition that would potentially cause an increase of $1 \text{ mS}\cdot\text{cm}^{-1}$ can be calculated. These values are presented in Table 5, along with model equations and the r statistic. The highly significant relationships between ECs and metal concentrations can be seen, as well as differences in CC of Cu or Cd required to elevate EC on each of the three soils. Consistent with other results, Cu had a greater effect on increasing EC than did Cd. Thus, effective rates of Cu addition were lower, for each $1 \text{ mS}\cdot\text{cm}^{-1}$ increase in EC,

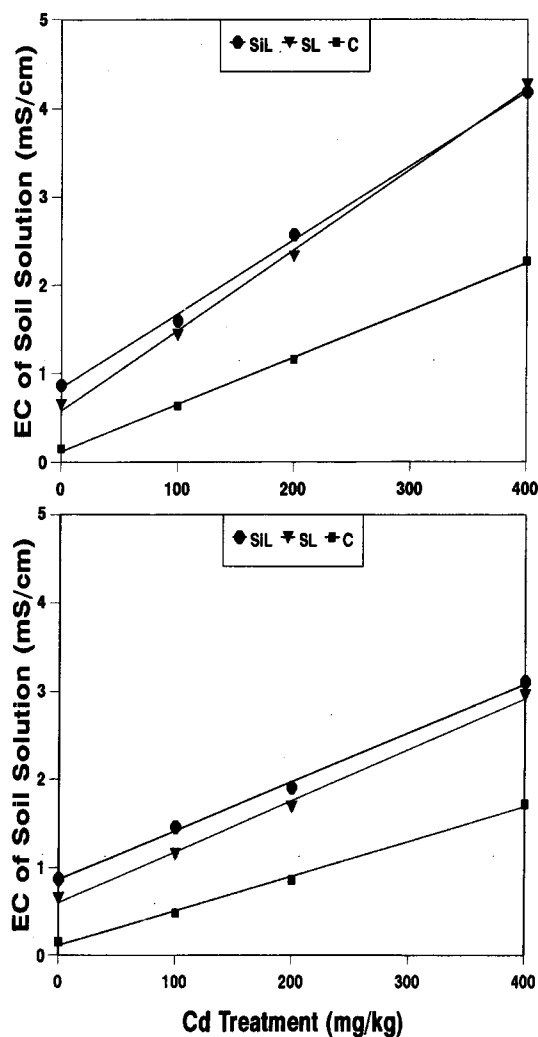


Fig. 5. Electrical conductivity (EC) of soil solutions as influenced by Cu or Cd additions in three soils.

than the rates of Cd additions. Soil differences were also large, with only $376 \text{ mg} \cdot \text{kg}^{-1}$ of Cu required to raise EC to $4 \text{ mS} \cdot \text{cm}^{-1}$ on the SL soil, but up to $732 \text{ mg} \cdot \text{kg}^{-1}$ on the C soil. In order to raise EC to $4 \text{ mS} \cdot \text{cm}^{-1}$, the estimated Cu concentration would be in the range of 330 to $730 \text{ mg} \cdot \text{kg}^{-1}$.

Quantity and Intensity relationship (buffering capacity).

The quantity/intensity relationship has been used as an indicator of soil nutrient supplying capacity,¹⁸⁾ where quantity (Q) is considered to be exchangeable cations and intensity (I) soluble cations in soil solution. The slope of this relationship can be considered as a measure of a soil buffer capacity for providing nutrient cations. Effects of heavy metal additions to three soils on Q/I parameters are presented in Table 6.

The buffer capacity of the SiL soil decreased as Cu or Cd application increased, due to adsorption of Cu or Cd and release of nutrient cations to soil solution (Fig. 2). Buffer capacities decreased about 60% with application of $100 \text{ mg Cu or Cd} \cdot \text{kg}^{-1}$. Results were similar in two other soils, but the magnitude of influence varied with soil properties. This relationship was linear for each soil, so we estimated CC of Cu or Cd required to decrease the initial BC by 50%, using the linear models. These varied according to soil texture, but again less Cu was required to induce the same effect as Cd, except for the C soil.

Discussion

When heavy metals are applied to soils, they may not be present in soil solution at concentrations strong enough to cause direct toxicity to plants or other organisms. Nevertheless, their presence may alter soil properties that are important for sustained productivity. The main objective of this study was to investigate indirect effects of Cu or Cd added to soils at increased rates. Three soils of different textures were treated with Cu or Cd in rates ranging from 0 to $400 \text{ mg} \cdot \text{kg}^{-1}$ of soil, and their nutrient supplying characteristics were evaluated. Little Cu or Cd was recovered in soil solution. Most of the added Cu was found to be in organically bound and residual forms, and most of the Cd was associated with Mn- and Fe-oxide fractions.

Soil solution pH decreased as addition of Cu or Cd increased, with changes of as much as 1.26 units from the highest addition of Cu. This magnitude of pH change could have significant effects on the solubility and availability of several nutrients. The distribution of cation nutrients

Table 5. Chemical concentrations of Cu or Cd (CC), estimated from the models between electrical conductivity (EC) and metal concentrations {[C]}, required to increase EC $\{(CC)_{ECn}\}$ to certain level (n).

Soils	Metals	Model equations	r	[Cu] or [Cd] at EC (mS/cm)			(CC) _{EC1} ^a
				1	2	4	
				----- $\text{mg} \cdot \text{kg}^{-1}$ -----			
SL	Cu	$EC=0.58+9.1 \cdot 10^{-3}C$	0.999***	46.3	156.1	376.0	109.9
	Cd	$EC=0.60+5.8 \cdot 10^{-3}C$	0.998***	68.9	241.4	586.2	172.4
SiL	Cu	$EC=0.84+9.6 \cdot 10^{-3}C$	0.999***	16.7	1238.6	329.2	104.2
	Cd	$EC=0.87+5.6 \cdot 10^{-3}C$	0.999***	24.1	204.3	559.6	178.6
C	Cu	$EC=0.12+5.3 \cdot 10^{-3}C$	0.999***	165.2	352.8	732.1	188.7
	Cd	$EC=0.10+4.0 \cdot 10^{-3}C$	0.998***	224.9	477.6	975.0	250.0

^aChemical concentrations of Cu or Cd required to increase $1 \text{ mS} \cdot \text{cm}^{-1}$ of EC.

***Significant at $p < 0.01$.

Table 6. Quantity (Q)/Intensity (I) relationships and chemical concentrations (CC) required to reduce the initial buffering capacity (BC) by 50%, estimated from models of BC vs metal concentrations ([C]).

soil	metal	TRT	Q/I relationships	r	BC vs concentration	r	CC _{BC50%} ^a mg·kg ⁻¹
SiL	Cu	control	Q=21.4+58.5 I	0.95	BC=58.1-17.2 log[C]	-0.99	48.7
		100	Q=20.4+23.4 I	0.99			
		200	Q=19.2+15.7 I	0.99			
		400	Q=16.3+16.1 I	0.99			
	Cd	control	Q=21.9+32.9 I	0.95			
		100	Q=21.6+13.2 I	0.86			
		200	Q=20.4+12.7 I	0.94			
		400	Q=18.9+10.0 I	0.90			
SL	Cu				BC=233.5-86.1 log[C]	-0.99	22.7
	Cd				BC=233.8-78.6 log[C]	-0.99	30.7
C	Cu				BC=295.8-95.8 log[C]	-0.96	34.9
	Cd				BC=263.9-86.3 log[C]	-0.98	33.9

^aChemical concentrations of metal to reduce the buffering capacity (BC) by 50%.

was also greatly influenced by heavy metal addition, with quantities of Ca and Mg in solution being directly related to rate of metal application. Solution concentrations of K and Na also increased, but to a smaller degree. As the soils were sequentially extracted after metals had been added, nutrient cation concentrations in solution decreased to very low levels, particularly after the third extraction.

The EC of the saturated soil pastes increased to levels considered to be detrimental to crop yields when Cu was added at a rate of 100 mg·kg⁻¹ or Cd at 200 mg·kg⁻¹. Soil buffer capacity for supplying cation nutrients was also decreased, with Cu having a greater effect than Cd. In all cases, less Cu was required to cause a certain level of influence on these parameters than Cd, suggesting that management criteria involving soil application of these metals to soils should include specific differences for each metal.

These results suggest that new protocols for assessing potential impacts of heavy metal additions in soils should be developed. Methods involving measurement of total or extractable metal concentrations do not provide the kinds of data that allow evaluation of indirect metal effects on soil characteristics that regulate sustainable productivity.

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