

Desorption of Copper from Some New Zealand Soils

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ABSTRACT

Availability of soil Cu to plants is dependent on the desorption into the soil solution of Cu from the surfaces of soil colloidal materials. Although there have been many studies of Cu sorption by soils, however, few have examined the process of Cu desorption. The objective of this study was to examine some of the factors likely to affect the desorption from soils of both native Cu and Cu added to soils. Ten New Zealand soils were used in this study and Cu desorption was determined by repeated equilibrations in 0.01 M Ca(NO₃)₂ solution. Desorption of native soil Cu varied between soils and the proportion of the total labile Cu in the soil (as determined by EDTA [ethylenediamine tetraacetic acid] extraction) that could be desorbed readily was strongly influenced by pH. Below pH 6.5, desorption increased with decreasing pH, and above pH 6.5 increased with increasing pH. When Cu was added to the soils (7 mg Cu kg⁻¹ soil) with an initial contact period between added Cu and soil of 24 h, <8.5% of the added Cu could be desorbed readily. The proportion of added Cu desorbed was reduced substantially by increasing the contact period to 12 wk before desorption. Desorption of native soil Cu was increased by increasing the temperature at which desorption was carried out. The effect of temperature on the desorption of added Cu differed between soils. The results of this study provide more evidence for the existence of slow reactions between added Cu and soil that reduce the ability of the Cu to desorb back into the soil solution.

IT IS NOW generally accepted that soil solution concentrations of micronutrients (and hence availability to plants) are probably controlled by sorption-desorption reactions at the surfaces of soil colloidal materials (Swift and McLaren, 1991). However, although numerous studies have examined the sorption of Cu by soils and soil components (McLaren and Crawford, 1973; Jarvis, 1981; McLaren et al., 1981; Raikhy and Takkar, 1981; Sanders, 1982), very few studies have examined the reverse process, i.e., desorption of Cu into solution. As noted by Swift and McLaren (1991), this is in some ways a paradox, since it is desorption processes that are likely to control the amount and rate of release of Cu (or other micronutrients) into solution for plant uptake. Of the few Cu desorption studies reported in the literature, most have examined desorption from individual soil components, e.g., McLaren et al., 1983; Padmanabham, 1983a. An exception to this is the study reported by Lehmann and Harter (1984), who examined the desorption kinetics of Cu applied to an intact soil. However our understanding of the factors affecting desorption of Cu from soils is far from complete. Such information is required in order to improve our ability to predict the release of both native Cu from soils and the release of Cu added to soils as a fertilizer or as a pollutant.

The objective of our study was to examine the de-

sorption of both native and applied Cu from a range of New Zealand soils. In particular, the effects of soil pH and temperature on Cu desorption were studied and, in the case of applied Cu, the effect of contact time between the Cu and the soil.

MATERIALS AND METHODS

Soils

Samples of topsoil (0–250 mm) were collected from 10 sites in New Zealand representing a wide range of soil types. The soils were selected to give a range in soil properties that were considered likely to influence the desorption behavior of soil Cu, e.g., organic matter, pH, clay, and Fe and Al oxide contents. The samples were air dried and ground to pass a 2-mm stainless steel sieve before use. The soils and some selected properties are listed in Table 1. The analyses shown in this table were carried out using the methods of Blakemore et al. (1987).

Desorption of Native Soil Copper

Desorption of Cu from soils was determined by repeatedly equilibrating samples of soil (5.0 g in duplicate) with 0.01 M Ca(NO₃)₂ (35 mL). Equilibrations were carried out for 2 h in polypropylene tubes on an end-over-end shaker at 20 °C. Preliminary studies indicated that there was little change in the amount of Cu desorbed from soil after the first 2 h of equilibration. After each 2-h equilibration period, the samples were centrifuged, and the supernatant solution decanted and filtered through a 5.0- μ m membrane filter. The soil was resuspended in fresh 0.01 M Ca(NO₃)₂ and the procedure repeated as necessary. The pHs of the desorption solutions were determined at the end of each 2-h desorption period and, for all soils, pH remained fairly constant during successive desorptions. These pH values, averaged for 10 desorption periods (pH_{DES}), were generally within 0.2 to 0.3 pH units of the soil pH values shown in Table 1.

Total Cu concentrations in the solutions were determined by atomic absorption spectrophotometry, using electrothermal atomization. Cumulative Cu desorption was calculated from the Cu concentrations in successive equilibration solutions.

Desorption of Added Copper

Samples of Lismore, Taupo, Temuka, and Waiareka soils (5.0 g in duplicate) were equilibrated at 20 °C for 24 h with 35 mL 0.01 M Ca(NO₃)₂ containing 1.0 μ g Cu mL⁻¹ (equivalent to 7.0 mg Cu kg⁻¹ soil). The concentration of Cu remaining in solution after 24 h was determined as described above and the Cu sorbed by the soil calculated by difference from the initial concentration. After decanting the original solution, the soils were resuspended in fresh Ca(NO₃)₂ and Cu desorption determined as described above.

Effect of Contact Time between Soil and Added Copper on Subsequent Desorption

For the Lismore and Temuka soils, in addition to an initial contact time of 24 h (as above), the experiment was repeated using contact times of 2 h, 4 wk, 8 wk, and 12 wk. Microbial activity was inhibited in the 4-, 8-, and 12-wk samples using 1 mL of 0.002% chlorhexidine.

For comparative purposes, samples of Lismore and Temuka soils without added Cu were also equilibrated with Ca(NO₃)₂

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Table 1. Selected properties of soils used in desorption studies.

Soil series	New Zealand soil group	U.S. soil taxonomy	pH (H ₂ O)	Organic C g kg ⁻¹	Oxalate Fe g kg ⁻¹	Oxalate Al g kg ⁻¹	Clay g kg ⁻¹
Craigieburn	Yellow-Brown Earth	Typic Dystrachrept	5.0	52	7	6	350
Lismore	Yellow-Brown Stony Soil	Umbric Dystrachrept	5.1	36	3	3	260
Takahe	Yellow-Grey Earth	Typic Fragiochrept	5.3	28	4	2	270
Taupo	Yellow-Brown Pumice Soil	Typic Vitrandept	5.0	82	4	12	200
Te Anau	Yellow-Brown Loam	Typic Haplumbrept	5.4	79	13	16	220
Templeton	Recent/Yellow-Grey Earth	Udic Ustrochrept	5.8	41	5	3	250
Temuka	Gley	Typic Haplaquept	5.6	59	4	4	420
Waiareka	Brown Granular Loam	Typic Hapludoll	6.5	78	11	10	410
Waikari	Rendzina	Udic Haplustoll	7.6	57	3	5	360
Waikuku	Yellow-Brown Sand	Typic Ustipsamment	4.6	22	1	1	110

for the above periods of time before Cu desorption was determined.

Effect of Temperature on Desorption

The desorption procedure described above for native soil Cu was repeated for the Lismore and Temuka soils using equilibration temperatures of 10 and 30 °C. These temperatures were also used to study desorption of added Cu (7 mg Cu kg⁻¹ soil) from these two soils after an initial contact time of 24 h at 20 °C.

Extractable Soil Copper

Samples of soil (5.0 g in duplicate) were shaken with 35 mL of 0.04 M EDTA on an end-over-end shaker at 20 °C for 24 h. The samples were centrifuged before the supernatant solution was filtered through a Whatman no. 41 filter paper.

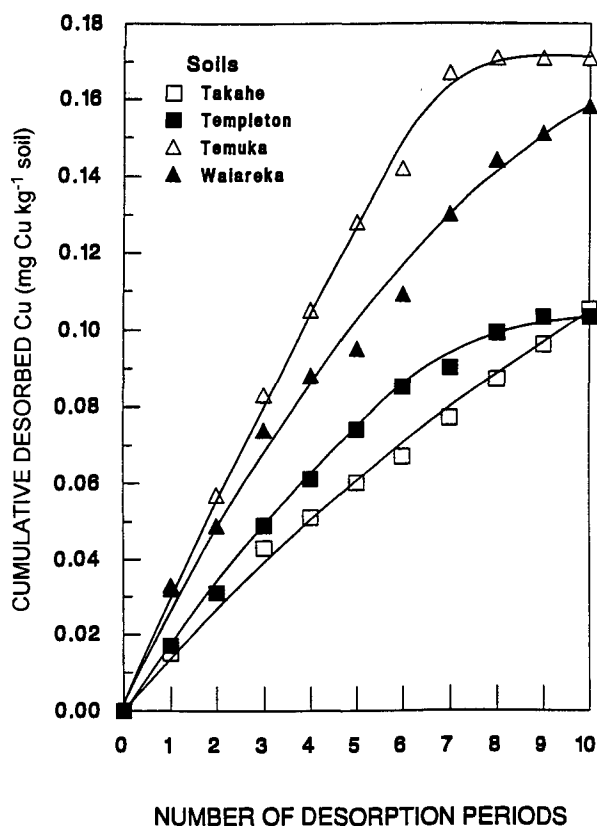


Fig. 1. Cumulative desorption of native soil Cu from some New Zealand soils.

Copper was determined in the filtrate by flame atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Desorption of Native Soil Copper

Figure 1 shows the cumulative amounts of native soil Cu desorbed from four of the experimental soils during 10 successive 2-h desorption periods. The amounts and patterns of desorption differed between the soils. The cumulative amount of native Cu desorbed ranged from 0.087 mg Cu kg⁻¹ for the Waikari soil up to 0.171 mg Cu kg⁻¹ for the Temuka soil (Table 2). For six of the experimental soils (Lismore, Taupo, Te Anau, Templeton, Temuka, and Waikari), the amounts of Cu desorbed were highest in the initial few periods and reached a plateau after six or seven desorption periods. The remaining four soils (Craigieburn, Takahe, Waiareka, and Waikuku), however, were still releasing measurable amounts of Cu at the completion of 10 desorption periods. These four soils appear to have a much more sustainable ability to release Cu into solution than the other soils examined.

It is interesting to compare the cumulative amounts of Cu desorbed after 10 equilibrations with Ca(NO₃)₂, with the amounts of Cu extracted from the same soils with EDTA. This reagent is widely used to estimate plant-available Cu in soils (Sims and Johnson, 1991), and may be considered an estimate of total labile soil Cu. In Table 2, the cumulative amount of Cu desorbed is expressed as a percentage of EDTA-extractable Cu for each of the soils. Except for the Waikuku soil, less than the equivalent of 30% of EDTA-extractable Cu could be desorbed

Table 2. Cumulative desorbed native soil Cu and ethylene diaminetetraacetic acid (EDTA)-extractable Cu concentrations.

Soil	Cumulative desorbed Cu†	EDTA-extractable Cu	Desorbed Cu as EDTA-Cu
	mg kg ⁻¹ soil	mg kg ⁻¹ soil	%
Craigieburn	0.17	0.92	18.3
Lismore	0.09	0.35	26.6
Takahe	0.11	0.82	12.8
Taupo	0.12	0.83	14.9
Te Anau	0.09	0.53	17.2
Templeton	0.10	2.71	3.8
Temuka	0.17	3.69	4.6
Waiareka	0.16	5.08	3.1
Waikari	0.09	1.33	6.5
Waikuku	0.16	0.33	48.5

† 10 desorption periods.

after 10 desorption equilibrations with $\text{Ca}(\text{NO}_3)_2$. For the Templeton, Temuka, Waiareka, and Waikari soils, <10% of the EDTA-extractable Cu values could be desorbed. Although EDTA is one of the extractants that has shown the most consistent success in predicting soil Cu availability to plants (Sims and Johnson, 1991), the comparison with the desorption data would suggest that extraction with this reagent overestimates the amount of readily plant-available Cu in soils. This is not surprising since EDTA extracts Cu predominantly from the organic fraction of the soil (McLaren and Crawford, 1973), much of which is probably not directly available to plants. In contrast, desorption of Cu into a dilute $\text{Ca}(\text{NO}_3)_2$ solution will depend not only on the total amount of labile Cu in the soil but also on other factors. These are likely to include the types, quantities, and relative proportions of soil components responsible for the retention of Cu in the soil, and the soil pH.

Attempts were made to relate the cumulative amounts of Cu desorbed from the soils to the above parameters. There was no statistically significant correlation between cumulative desorbed Cu and EDTA-extractable Cu or with any of the other soil properties shown in Table 1. However, the cumulative amount of Cu desorbed (10 desorptions) expressed as a percentage of EDTA-extractable Cu did appear to be related to pH_{DES} . This relationship was described well (significant at $P < 0.005$) by a second-order polynomial equation that shows a decrease in desorption with increasing pH, reaching a minimum at approximately pH 6.5, followed by an increase in desorption above this pH (Fig. 2). Although there was only one data point above pH 6.5, it is considered that the fitted data trend is realistic. Copper solubility in soils has been shown to increase at both low and high pH values (McBride and Blasiak, 1979; Swift and McLaren, 1991).

The increase in desorption with decreasing pH below 6.5 is similar to the trend observed by Padmanabham (1983a), when studying the desorption of Cu from goethite, an Fe oxide commonly found in soils. Padmanabham (1983a) proposed the existence of specific sites in goethite, which are responsible for the irreversible (or very slowly reversible) sorption of Cu and showed that the proportion of such sites increased with pH. Cavallaro and McBride (1984) have also shown that desorption of Cu from soil clays decreases with an increase in pH.

The fact that desorption of Cu from the soil labile Cu pool is influenced by pH clearly has implications for the uptake of soil Cu by plants. Desorption data on its own, however, will not necessarily provide an effective measure of soil Cu availability. Many other factors in addition to purely physico-chemical ones are also involved, not least the plant itself and its influence on the root environment.

Desorption of Added Soil Copper

All four soils used in this part of the study sorbed virtually all (>98%) of the added Cu (7 mg Cu kg^{-1} soil) during the initial 24-h equilibration period. Subsequent successive desorptions from the soils resulted in large increases in the amounts of Cu desorbed compared with samples where native Cu only was present, e.g., the Lismore and Taupo soils, Fig. 3. For all four soils, however, the proportions of added Cu desorbed during 10 desorption periods were extremely low, ranging from

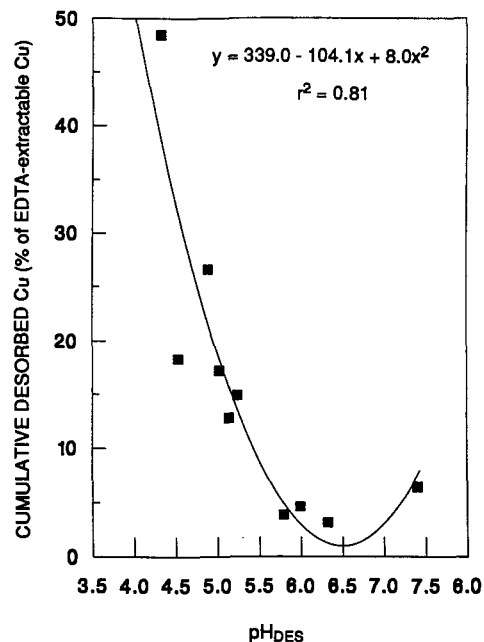


Fig. 2. Relationship between cumulative desorbed native soil Cu (10 desorption periods) and the mean pH of the desorption solution (pH_{DES}).

2.4% for the Waiareka soil to 8.3% for the Taupo. This relatively low desorption of added Cu occurred even though the initial contact period between the added Cu and the soil had been relatively short (24 h).

The low proportions of added Cu desorbed from the soils agrees with the results of previous studies with individual soil components. Sorption of Cu by a range of soil components has been shown to be largely irreversible or only slowly reversible (McLaren et al., 1983; Padmanabham, 1983a,b; McBride et al., 1984). Various hypotheses have been put forward to explain this type of behavior. McBride (1991) stated that activation energies for desorption may be much larger than those for sorption, and rates of sorption at ambient temperature are likely to be much faster than desorption rates. Thus the low proportions of added Cu desorbed in this and other studies may reflect, in part, nonequilibrium conditions caused by slow desorption rather than true irreversibility. Barrow (1985) has also indicated that initial sorption reactions may be followed by slower reactions that would render a proportion to the sorbed Cu unavailable for immediate equilibrium with the soil solution. It is uncertain, however, whether such reactions are likely to be of importance for a relatively short sorption period of 24 h.

Although such small proportions of the added Cu were desorbed during 10 desorption equilibrations, it should be noted that at the end of this period Cu was still being desorbed (Fig. 3). It might be expected that, with time, greater amounts of the added Cu could be desorbed back into solution and therefore be considered to remain available for plant uptake.

Effect of Contact Time on Desorption of Added Copper

A preliminary experiment (data not shown) was carried out that compared desorption of applied Cu from

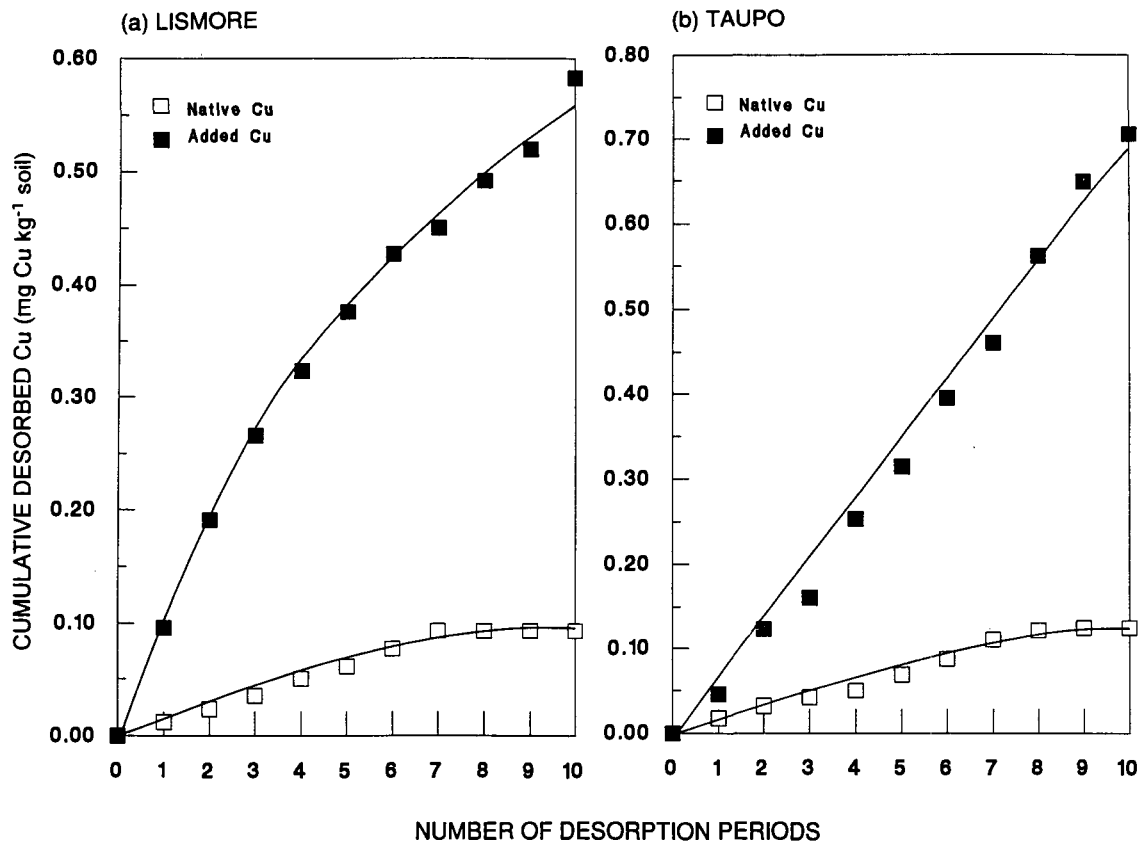


Fig. 3. Cumulative desorption of native and added Cu from Lismore and Taupo soils (added Cu treatment = 7 mg Cu kg⁻¹ soil).

the Waiareka soil after an initial sorption period of 2 h, with the desorption obtained after a 24-h sorption period. At the completion of 10 desorption periods, although the difference was not large numerically, significantly more Cu had been desorbed from the soil that had been in contact with the added Cu for the shorter period of time (3.3% of the added Cu compared with 2.4%).

As a result of this preliminary study, a longer term experiment was carried out with the Lismore and Temuka soils using initial contact periods of 4, 8, and 12 wk before desorption of the added Cu was measured. Figure 4 shows clearly that, for both soils, the amount of Cu desorbed declined with increasing contact time between the added Cu and the soil. These results are in general agreement with the trends reported for Cu desorption from goethite by Padmanabham (1983a) and from soil by Lehmann and Harter (1984). In both of these studies, the longer the period between the initial sorption of Cu and the start of desorption, the greater the amount of Cu that was irreversibly sorbed. The nature of the slow reactions that result in this decrease in desorption of added Cu remains open to conjecture. Solid diffusion into mineral lattice structures has been suggested, but McBride (1991) pointed out that such reactions would be extremely slow indeed. It would appear more likely that, with increased time of sorption, there is a slow redistribution of Cu ions to more strongly binding or less accessible sites, possibly involving diffusion into extremely small pores and interparticle spaces. Although the actual amounts of Cu involved in these slow reactions appear to be small compared with the total amounts of Cu sorbed, they do represent a considerable

proportion of the Cu that can initially be desorbed from the soil. Therefore, the corresponding effects on plant availability of added Cu could also be significant.

For comparison purposes, samples of Lismore and Temuka soils without added Cu were also equilibrated in Ca(NO₃)₂ for periods of 4, 8, and 12 wk before Cu desorption was determined. The results of these controls are also shown in Fig. 4. Somewhat unexpectedly, native soil Cu also showed a decrease in desorption with increasing time of initial equilibration. It might be thought that native soil Cu would be in an equilibrium state and continuing reactions with soil components was unlikely. In common with other nutrients, however, Cu will be continually cycled in the soil through decaying organic materials and, through eventual mineralization, a pool of Cu ions will be maintained that has not had time to react irreversibly with the soil. Interruption of nutrient cycling (by sampling the soil) will stop the supply of Cu from this source and Cu already present in soluble or sorbed forms will gradually be subject to the slow reactions discussed above. It also seems likely, however, that the nature of the equilibration process in Ca(NO₃)₂ at a wide solution/soil ratio creates conditions favorable for the slow reactions to take place. The rates at which such reactions occur in soils at normal soil moisture contents is probably much slower than those observed in soil suspensions in the laboratory. Evidence that slow reactions between Cu and soil do also occur in field-moist soils has been obtained by Williams and McLaren (1982). These workers showed that during a period of 44 wk, EDTA extractability of both native and added Cu declined in soils incubated under field-moist conditions.

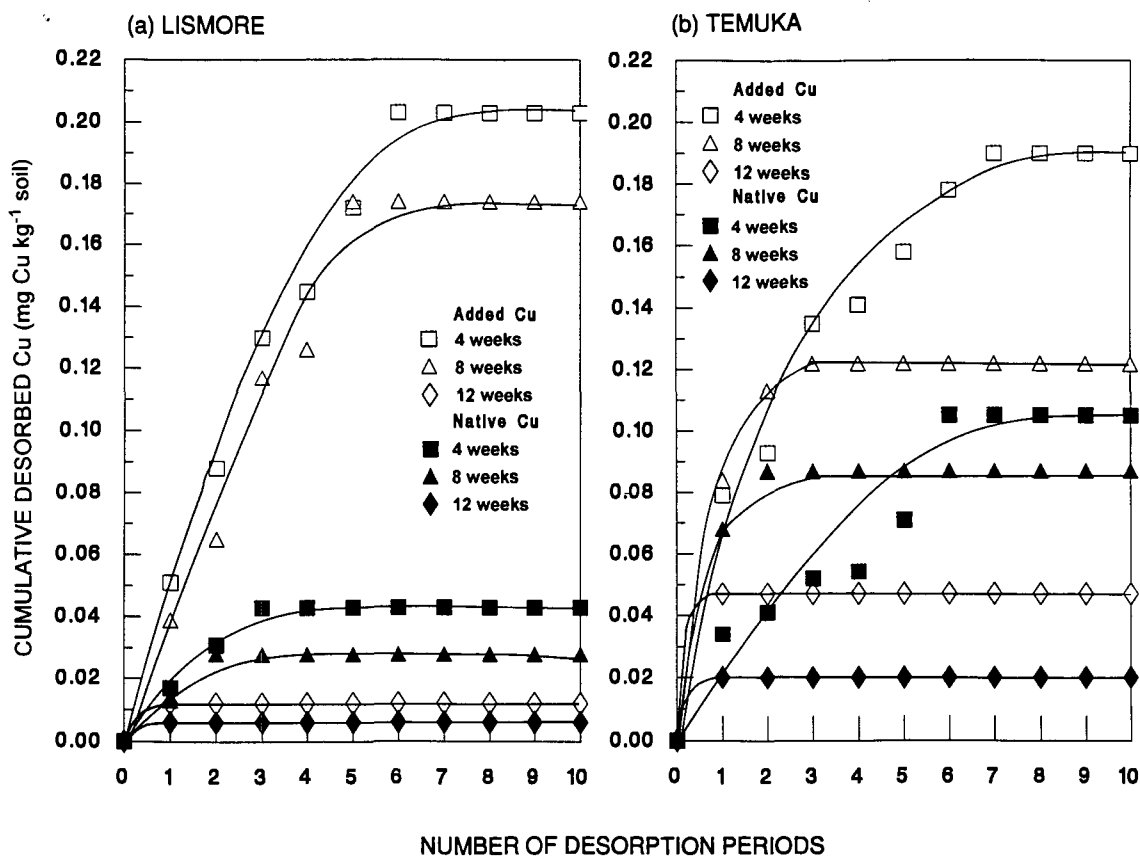


Fig. 4. Cumulative desorption of native and added Cu from Lismore and Temuka soils following initial equilibration periods of different lengths.

Fox (1992), in field experiments with a range of soils, has also shown a decrease with time in the extractability of Cu applied as a fertilizer.

Effect of Temperature on Copper Desorption

For both the Lismore and Temuka soils, the amount of native soil Cu desorbed (11 desorption periods) increased with increasing temperature of equilibration (Fig. 5). Such an effect would be expected if, as stated by McBride (1991), desorption requires a significant activation energy.

The effect of increasing temperature of equilibration on the desorption of added Cu differed between the two soils. With the Lismore soil, the cumulative amount of added Cu desorbed decreased with increasing temperature (Fig. 5), i.e., the reverse of what occurred with native soil Cu. With the Temuka soil, there was little difference between the amounts of Cu desorbed at the three equilibration temperatures.

The results for added Cu can be explained by considering the effect of temperature not just on the desorption process itself, but also on the slow reactions that gradually decrease the ability of added Cu to desorb back into solution. In view of the results described above, it is likely that these slow reactions would have been continuing during the time taken to carry out the desorption equilibrations. The rate of these reactions, particularly if diffusion processes are involved, would be expected to increase with an increase in temperature. Thus the over-

all effect of temperature on the desorption of added Cu will be a net effect of temperature on desorption (desorption increasing with temperature as observed for native soil Cu) and on the slow reactions (Cu available for desorption decreasing with temperature). In the case of the Lismore soil it would appear that the effect of temperature on the slow reactions was the dominant effect and thus the net effect was a decrease in desorption with increasing temperature (Fig. 5a). With the Temuka soil the effects of temperature on the two types of process appeared to be balanced, with no marked net effect of temperature on desorption (Fig. 5b). The difference between the soils is no doubt related to differences in properties between the two soils. For example, the Temuka soil had higher organic C, Fe and Al oxide, and clay contents than the Lismore soil; it also had a higher pH value (Table 10).

CONCLUSIONS

The amount of Cu that can desorb readily from soil depends not only on the total amount of labile Cu in the soil but also on soil pH, temperature, and, in the case of added Cu, on the length of time since addition of the Cu to the soil. The observations made in this study provide additional evidence for the existence of slow reactions that reduce the ability of Cu sorbed by soils to desorb readily back into solution. The occurrence of such reactions clearly has implications for the long-term availability to plants of Cu added to soils as fertilizer or as a pollutant.

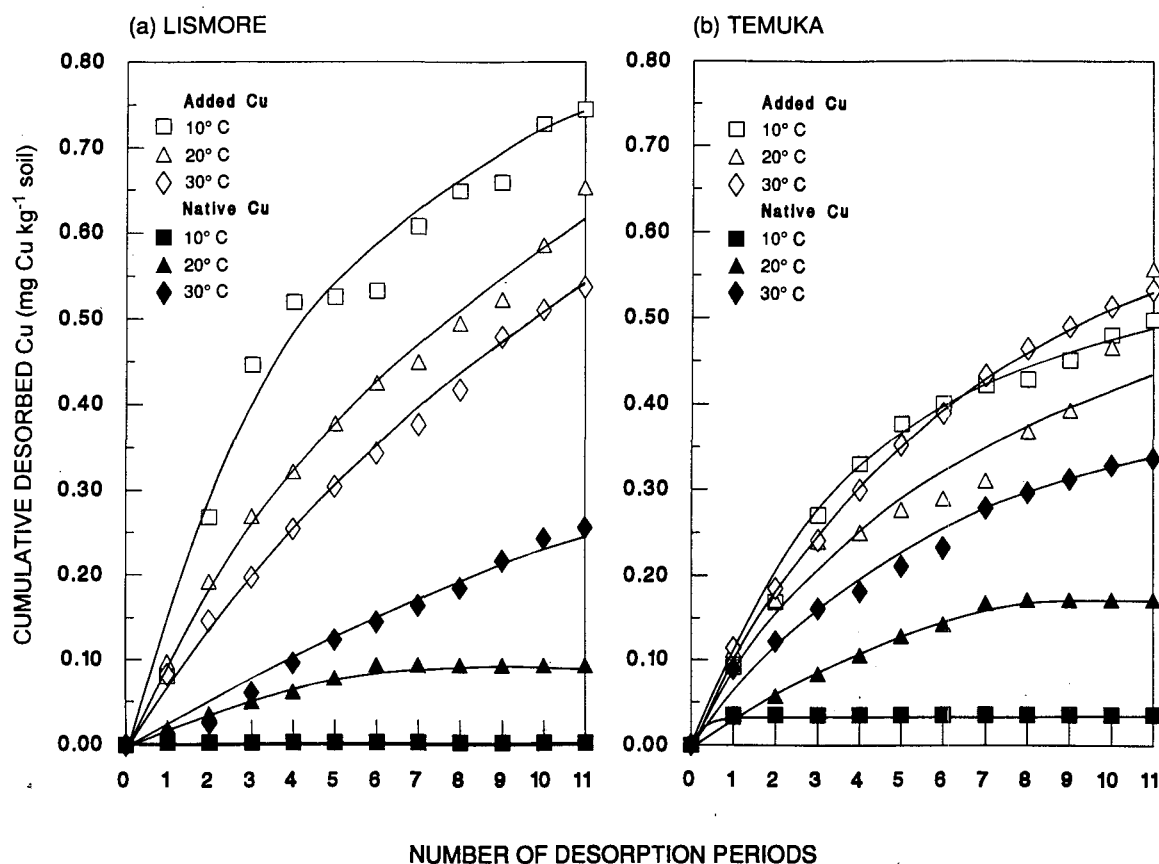


Fig. 5. Cumulative desorption of native and added Cu from Lismore and Temuka soils at different temperatures.

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