Mobility of Copper Fertilizers in Soils

P.L. Flaten[1], F.L. Walley[2], R.E. Karamanos[3]

[1,2]Saskatchewan Centre for Soil Research, Univ. of Sask., Saskatoon, SK, S7N 5A8
[3]Westco, Box 2500, Calgary, AB T2P 2N1

Key Words: copper, micronutrient, wheat, EDTA, sulphate, mobility

Introduction

Due to its cationic nature, Cu mobility is assumed to be very limited in Prairie soils, which are dominated by negatively charged constituents (McLaren et al., 1983). Clay and organic matter are major sources of these negatively charged surfaces. Root interception, therefore, plays an important role in plant uptake of Cu. Normally, where Cu fertilizer applications are required to correct a deficiency, proximity to growing roots is considered essential (Gilkes and Sadleir, 1979).

Incorporation of surface broadcast copper sulphate ($CuSO_4$) has been an effective practice. However, over the past decade, there has been a significant shift towards less tillage and an increased awareness of other products and methods of application.

Chelating agents are added to nutrient solutions to increase the solubility of metal cations. Metal chelates are characterized by the formation of more than one bond between the metal and functional groups of the complexing agent, forming a ring structure incorporating the metal ion. One of the most common chelating agents used for this application is EDTA (ethylene diamine triacetic acid). The relatively high stability of this product in chemical reactions is seen as an advantage for maintaining the availability of the nutrient.

The objective of this experiment was to identify the relative mobility of Cu, using two fertilizer products, namely, $CuSO_4$ (salt) and Cu-EDTA (chelate).

Materials and Methods

Copper mobility was investigated in five homogenous surface soils (0-10 cm), using a column experiment. Soils were collected in Saskatchewan and Alberta and represented a variety of organic matter and clay contents (Table 1).

Soil column sleeves were 15 cm long x 9 cm diameter, constructed of plastic liners with vinyl caps as seen in Figure 1. Filter paper and greenhouse plastic beads were used as a filtering system, with drainage provided by tipless syringes inserted through vinyl caps. Soils were evenly packed in columns to a depth of 10 cm, according to reasonable bulk densities for each texture (see Table 1). Treatments were replicated four times and columns were arranged in a completely randomized design.

Table 1. Physico-chemical Properties of Soils used in the Cu Mobility Experiment.

Soil Association	Sand (%)	Silt (%)	Clay (%)	Texture	Organic C (%)	pH	B.D.[†] (g/cm3)
Sylvania	77.7	18.2	4.1	Loamy Sand	0.2	5.1	1.4
Meota	81.1	12.6	6.2	Loamy Sand	1.6	7.4	1.4
Waitville	33.7	53.4	12.9	Silt Loam	2.1	6.7	1.2
Oxbow	33.8	43.5	22.7	Loam	5.0	6.9	1.1
Malmo	10.4	54.7	34.9	Silty Clay Loam	10.8	6.7	0.9

[†] Note: Bulk densities used to pack columns with dry soil.

Figure 1. Column apparatus used in the copper mobility experiment.

Experiment and Sample Collection

The experiment was carried out at room temperature. Columns were pre-wetted from above with pulses of 2 cm of deionized distilled water until leachate broke through the base of the column. Columns were allowed to equilibrate for 12 h prior to Cu application.

Three treatments were applied to the surface of the columns:
1) Control - 5 ml of water;
2) Cu sulphate - 12.7 mg Cu diluted with deionized distilled water to 5 ml solution;

3) Cu chelate (Cu 7.5% EDTA, fully chelated) - 12.7 mg Cu diluted with deionized distilled water to 5 ml solution.

Copper treatments were applied to the column surface at a rate equivalent to 20 kg Cu ha^{-1} (approximately 10 mg Cu kg^{-1}). Pulses of 2 cm of 0.01M CaCl solution were added to each column every day for 10 days. Leachate from each column was collected each day and analyzed for total Cu concentration. At the completion of the experiment, soil columns were sliced into 1 cm increments and analyzed for DTPA-extractable Cu, which represents plant-available Cu.

Results

Copper found in leachate: Copper was not detected in the leachate of soils treated with Cu sulphate (Tables 2 and 3). However, Cu, when applied as Cu chelate, leached through all five soils (Fig. 2). The Meota and Sylvania soils, representing the soils with lowest clay and organic matter contents, allowed more Cu to leach through than the other soils. The Malmo soil, representing the soil with greatest clay and organic matter content, allowed the least Cu to flow through. Where Cu chelate was applied, Cu was detected in the leachate within the first day of application. Recovery typically was maximized within 3 d of application after which little or no additional Cu was leached through the soil.
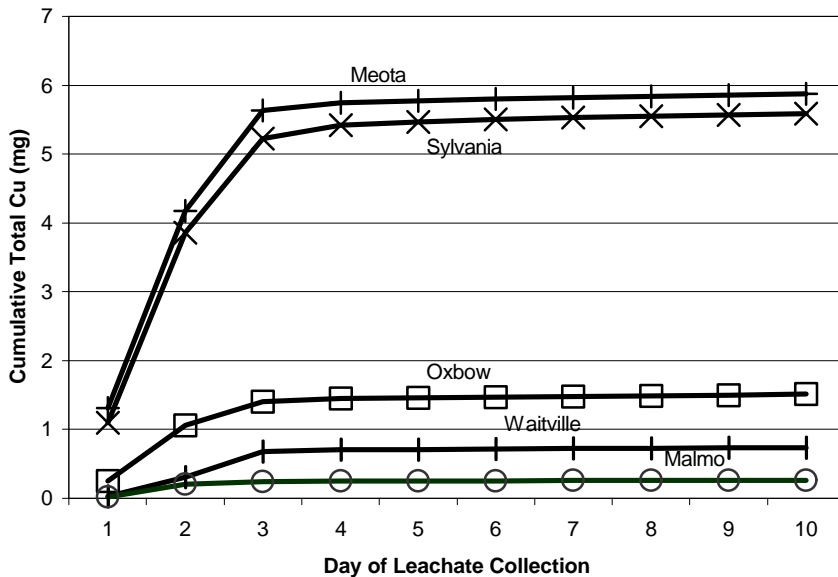

Figure 2. Cumulative total Cu found in leachate of five soils over a 10-day period following application of Cu chelate.
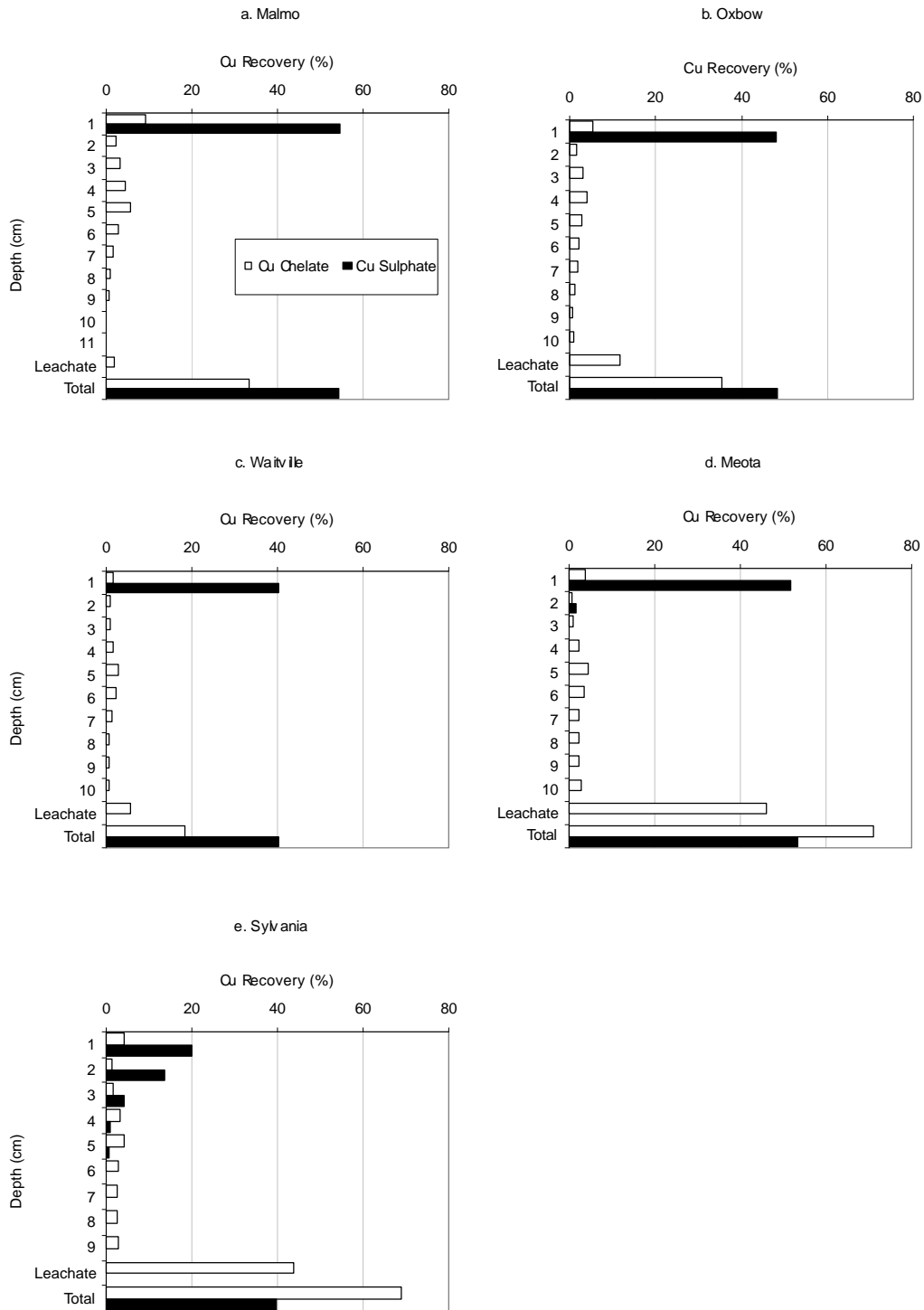
Figure 3. Mean Percent recovery of copper found in soil, by depth, and leachate for five soils: a) Malmo b) Oxbow c) Waitville d) Meota e) Sylvania.

The analysis of DTPA-extractable Cu in the soils, by depth is represented in Fig. 3 and Tables 2 and 3. Differences in the final height of the columns were due to variable expansion and compaction of the soils on wetting. When applied as $CuSO_4$, Cu was strongly associated with the surface of all soils although some Cu was detected below the surface in the Meota and Sylvania soils. The Sylvania soil, in particular, behaved quite differently relative to the other soils. Under the $CuSO_4$ treatment, extractable Cu was detected in significant though progressively lesser amounts in lower depths, to a maximum depth of 7 cm. Total recovery, calculated as Cu detected in both leachate and the soil divided by the amount applied, indicated that approximately 40 to 55% of the Cu applied as $CuSO_4$ was measured by analysis.

When applied in chelate form, Cu was detected in all depths of all soils. Where total recovery was high, it reflects the degree to which Cu was found in the leachate, the range of which approximates 20 to 70%. No strong association between Cu and the surface layer is seen in the soil-Cu data under the chelate treatment.

Discussion

Copper sulphate: The behavior of Cu in this experiment, applied as $CuSO_4$, confirms previous work describing Cu as strongly adsorbing to clay and organic matter, and therefore, having restricted mobility (Jones and Belling, 1967). The relative degree of movement of Cu in various soils was clearly related to the amounts of clay and organic constituents in each of the soils. The high degree of Cu movement in the Sylvania soil can be attributed to the extremely low contents of clay, organic matter and possibly the low pH. Given the data provided, it is impossible to separate the impact of clay versus organic matter, since the relative magnitude of each is identical in these soils.

Within the short period of this experiment, 46 to 60% of the amount of Cu applied is unrecoverable and deemed 'unavailable' according the DTPA extraction method. It can be assumed that with extended time more Cu would become unavailable as a consequence of sorption processes. It is possible that the Cu that has become unavailable, particularly in soils other than those represented by the characteristics of the Sylvania soil (low clay and organic matter), will not readily return to the available fraction.

Copper chelate: Copper, applied as Cu chelate, behaves in a manner similar to $CuSO_4$ in terms of its relative mobility depending on soil characteristics. However, the degree of movement through all of the soils reflects the designed behavior of the chelated product. The effectiveness of chelates as metal carriers in soils depends on their ability to keep these metals in soluble, mobile forms (Lindsay and Norvell, 1969). The results of this experiment demonstrate that EDTA was effective in allowing a portion of the Cu to leach through the 10 cm column of soil. The size of that portion appears to be related to the same soil qualities as restricted the Cu applied as $CuSO_4$ (i.e., texture and organic matter content), with the sandiest soils of least organic matter allowing more Cu through.

Copper was detected in the leachate of the Cu chelate treatment on the first day, essentially reaching maximum cumulative levels by the third day of the experiment. The sudden absence of Cu in the leachate from all of the soils indicates that a change had occurred in that product by

that time, as the leachate-Cu dis not account for the full amount of Cu applied. In fact, when the total leachate and total DTPA-extractable Cu were summed, there was still 29 to 67% of the applied Cu unaccounted for. Of the Cu remaining in the soil, DTPA extractable Cu amounted to only 13-46% of the applied Cu remaining in the soil. We also do not know how much of the leachate-Cu would have remained in an extractable form in the soil if it had not been removed from the soil environment. It may be possible to explain the fate of the Cu chelate according to the stability of Cu-EDTA.

The stability of the metal-ligand bond generally determines solubility and therefore availability of the applied nutrient (Mortvedt and Cox, 1985). In soil solutions, EDTA exists in equilibria with a variety of cations. An effective chelate is one for which the ligand must remain in solution and must continue to complex the applied Cu. In this experiment, the Cu-EDTA has possibly exchanged Cu^{2+} for Fe^{3+} or Ca^{2+} in soil solution (Norvell, 1991). These exchanges would then allow the Cu^{2+} to adsorb to clay or organic matter constituents. That which is specifically adsorbed would then be strongly held and therefore likely not reclaimed as part of the 'available fraction' represented by the DTPA method of extraction.

Agronomic Implications

The results of this experiment provide several agronomic implications. It confirms that $CuSO_4$ can normally be thought of as non-mobile and therefore must be placed within the root zone of plants in order to expect effective uptake. Where $CuSO_4$ is broadcast, it should also be incorporated. Seed placed applications of granules may be ineffective due to sporadic placement of granules at recommended low rates and lack of mobility. Only in cases of extremely low clay and organic matter soils would there be some potential for Cu mobility, possibly making root zone placement less necessary.

Copper chelate, on the other hand, has potential for movement with water to the root zone in the full range of soils studied. Therefore, root zone placement may not be necessary. However, since mobility was hindered within three days of application, this form of Cu will also become non-mobile.

Table 2. Mean Percent Recovery of Applied Copper in Soil and Leachate in Five Soils.

Depth	Malmo	Meota	Oxbow	Sylvania	Waitville	Malmo	Meota	Oxbow	Sylvania	Waitville
			Cu-EDTA					$Cu\ SO_4$		
(cm)			Recovery (%)					Recovery (%)		
1	9.30[†]	3.90	5.43	4.00	1.47	54.55	51.88	48.01	19.84	40.22
2	2.34	0.78	1.45	1.41	0.98	0.09	1.47	0.19	13.65	0.19
3	3.23	0.88	3.01	1.56	0.86	0.02	0.00	0.03	4.12	0.01
4	4.53	2.19	3.99	3.19	1.49	-0.04	0.02	-0.13	1.05	-0.01
5	5.56	4.52	2.83	4.01	2.77	0.13	-0.02	-0.03	0.52	0.01
6	2.91	3.60	2.29	2.94	2.19	-0.08	-0.02	0.08	0.29	0.01
7	1.48	2.12	1.97	2.48	1.22	-0.08	-0.02	-0.02	0.10	0.00
8	0.92	2.12	1.11	2.57	0.55	0.07	0.01	0.06	0.02	0.02
9	0.57	2.12	0.74	2.91	0.57	0.12	0.00	-0.09	0.02	-0.01
10	0.26	2.79	0.93		0.53	-0.27	0.03	0.11		-0.04
11	0.21					-0.23				
Total Soil	31.31	25.02	23.73	25.07	12.63	54.28	53.34	48.20	39.61	40.40
Total Leachate	1.89	46.12	11.80	43.84	5.69	0.01	-0.02	0.02	0.00	0.00
Total Recovery	33.20	71.14	35.53	68.92	18.32	54.29	53.32	48.22	39.60	40.40
Not recovered	66.80	28.86	64.47	31.08	81.68	45.71	46.68	51.78	60.40	59.60

[†] Data represents percent recovery of copper in soil treated with copper subtracting the Cu detected in control soil.

Table 3. Mean Recovery (mg) of Applied Copper in Soil and Leachate in Five Soils.

Depth	Malmo	Meota	Oxbow	Sylvania	Waitville	Malmo	Meota	Oxbow	Sylvania	Waitville
	----------------------- Cu-EDTA -------------------------					------------------------- Cu SO_4 -------------------------				
(cm)	Recovery (mg)					Recovery (mg)				
1	1.18[†]	0.49	0.69	0.51	0.19	6.93	6.59	6.10	2.52	5.11
2	0.30	0.10	0.18	0.18	0.12	0.01	0.19	0.02	1.73	0.02
3	0.41	0.11	0.38	0.20	0.11	0.00	0.00	0.00	0.52	0.00
4	0.57	0.28	0.51	0.40	0.19	-0.01	0.00	-0.02	0.13	0.00
5	0.71	0.57	0.36	0.51	0.35	0.02	0.00	0.00	0.07	0.00
6	0.37	0.46	0.29	0.37	0.28	-0.01	0.00	0.01	0.04	0.00
7	0.19	0.27	0.25	0.32	0.16	-0.01	0.00	0.00	0.01	0.00
8	0.12	0.27	0.14	0.33	0.07	0.01	0.00	0.01	0.00	0.00
9	0.07	0.27	0.09	0.37	0.07	0.01	0.00	-0.01	0.00	0.00
10	0.03	0.35	0.12		0.07	-0.03	0.00	0.01		-0.01
11	0.03					-0.03				
Total Soil	3.98	3.18	3.01	3.18	1.60	6.89	6.77	6.12	5.03	5.13
Leachate	0.24	5.86	1.50	5.57	0.72	0.00	0.00	0.00	0.00	0.00
Total Recovery	4.22	9.04	4.51	8.75	2.32	6.89	6.77	6.12	5.03	5.13
Not Recovered	8.48	3.66	8.19	3.95	10.38	5.81	5.93	6.58	7.67	7.57
% Exch Cu in Col[‡]	31.91	46.45	26.91	44.66	13.39	54.28	53.34	48.20	39.60	40.40

[†] Data represents percent recovery of copper in soil treated with copper subtracting the Cu detected in control soil.

[‡] Percent of Cu remaining in the soil (not found in leachate) that remains available, as measured by the DTPA extraction method.

References:

Gilkes, R.J., and S.B. Sadleir. 1979. The influence of placement geometry on the effectiveness of copper superphosphate. Aust. J. Soil Res. 17:121-128.

Jones, G.B., and G.B. Belling. 1967. The movement of copper, molybdenum, and selenium in soils as indicated by radioactive isotopes. Aust. J. Agric. Res. 18:733-740.

Lindsay, W.L., and W.A. Norvell. 1969. Equilibrium relationships of Zn^{2+}, Fe^{3+}, Ca^{2+}, and H^+ with EDTA and DTPA in soils. Soil Sci. Soc. Am. J. 33:62-68.

McLaren, R.G., J.G. Williams, and R.S. Swift. 1983. Some observations on the desorption and distribution behaviour of copper with soil components. J. Soil Sci. 34:325-331.

Mortvedt, J.J., and F.R. Cox. 1985. Production, marketing, and use of calcium, magnesium, and micronutrient fertilizers, p. 455-482, *In* O. P. Engelstad, ed. Fertilizer Technology and Use, Third ed. Soil Science Society of America, Inc., Madison, Wisconsin, USA.

Norvell, W.A. 1991. Reactions of metal chelates in soils and nutrient solutions, p. 187-228, *In* J. J. Mortvedt, et al., eds. Soil Science Society of America Book Series, 2nd ed. Soil Science Society of America, Inc., Madison, Wisconsin, USA.