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Examining the fixation kinetics of chelated and non-chelated copper and the applications to micronutrient management in semiarid alkaline soils

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Abstract. This study examined and compared the fixation and fixation kinetics of copper (Cu) in chelated (ethylene diamine tetraacetic acid, EDTA) and non-chelated mixed systems of micronutrients in the semiarid soils of the Southern High Plains, USA, using findings from Cu extraction studies and kinetic models. Approximately, 22 % more Cu was fixed in the non-chelated system compared to the chelated within the first 14 days with only 7 % difference between the two systems by day 90. Findings suggest a decrease in the effectiveness of chelated micronutrients over time, highlighting the significance of timing even when chelated micronutrients are used. The strengths of the relationship of change in available Cu with respect to other micronutrients (iron (Fe), manganese (Mn), and zinc (Zn)) were higher in the non-chelated system (R^2: 0.68–0.94), compared to the chelated (R^2: 0.42–0.81), with slopes of 0.40 (Cu–Fe), 0.31 (Cu–Mn), and 1.04 (Cu–Zn) in the non-chelated system and 0.26 (Cu–Fe), 0.22 (Cu–Mn), and 0.90 (Cu–Zn) in the chelated system. Reduction in the amount of available Cu was best described by the power function model ($R^2 = 0.91$, $\mathrm{SE} = 0.081$) in the non-chelated system and second-order model ($R^2 = 0.95$, $\mathrm{SE} = 0.010$) in the chelated system. The applications generated from this study could be used as tools for improved micronutrient management and also provide baseline data for future work in other semiarid/arid alkaline soils of the world. Findings are also more applicable to field settings, an improvement over related previous studies.

1 Introduction

Malnutrition resulting from lack of adequate micronutrients in foods, a situation that could be partly attributed to the ease of micronutrient fixation in soil systems, contributes significantly to the global burden of disease (WHO, 2000). The fate of the plant-available portion of micronutrients is controlled by a number of soil factors including soil pH, organic matter (OM), texture, aeration status, calcium carbonate ($CaCO_3$), iron (Fe) oxides, and interaction with other micronutrients, etc. (Havlin et al., 2013; Fernández-Calviño et al., 2013). Plant availability of micronutrients could be a bigger challenge in calcareous or alkaline soils due to their high pH (Rashid and Ryan, 2004; Alloway, 2008). High soil pH leads to decreased solubility and increased fixation of most micronutrients such as copper (Cu), zinc (Zn), Fe, and manganese (Mn) in such soils, leading to reduction in the plant-available portion (Sparks, 2003; Havlin et al., 2013). For Cu, apart from pH, reduction in availability resulting from its interaction with OM functional groups, particularly in soils treated with organic amendments such as animal manure and biosolids, has also been well documented (De Schamphelaere et al., 2004; Pinto et al., 2004). Its availability has also been reported to increase with soil OM (under moderate OM level) and clay content, and to decrease with an increase in pH and $CaCO_3$ (Alloway, 2008). Interactions among nutrients resulting in antagonism are also common (Dimkpa et al., 2013; Havlin et al., 2013; Bindraban et al., 2015), for instance, plant uptake of Cu is shown to be reduced by ele-

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vated soil concentrations of other micronutrients such as Zn and Fe, as well as the macronutrient phosphorus (P) (Havlin et al., 2013).

Given the aforementioned challenges, to increase the availability of micronutrients such as Cu to plants, they are preferably applied in the form of synthetic and organic chelates. The advantages of the chelated forms have also been documented under certain soil types and conditions by a number of researchers (Kayser et al., 2000; Sekhon, 2003; Luo et al., 2005; Chiu et al., 2005). However, the heterogeneous nature of soil limits the extension of findings from one soil type to another among regions, thus, often necessitating site-specific studies.

The soils of the Southern High Plains (SHP) of the USA are of the semiarid climate and are characteristically alkaline in nature. As can be likened to other arid to semiarid regions of the world (Amuti et al., 2014; Sarah and Zonana, 2015; Torres et al., 2015; Barbero-Sierra et al., 2015; Mureithi et al., 2015), this region (the SHP) is currently facing complex environmental challenges such as drought, declining groundwater quality, wind erosion, and soil salinization that limit agricultural productivity (Mehta et al., 2000; Stout, 2001; Allen et al., 2005; Young et al., 2015). Recent observations have also revealed an increasing number of cases of micronutrient deficiency, which could be attributed to the characteristically high pH soils prevalent in this region and intensive crop production activities. Unfortunately, little to no information is available on the chemistry of micronutrients in the semiarid alkaline soils of this region, despite the agronomic significance of these soils. Understanding the kinetics of plant-available micronutrient fixation in these soils is vital for developing improved nutrient management plans for agricultural and environmental sustainability. Kinetic parameters obtained can be used for comparisons among micronutrients and among soils. A systematic approach to examining the chemistry of micronutrients in soil systems will encompass the examination of the chemistry of these micronutrients in a mixed system (of a number of other micronutrients).

Although a number of studies have examined the kinetics of micronutrient fixation in soils (Manouchehri et al., 2006; Reyhanitabar and Gilkes, 2010; Abbas and Salem, 2011), the experimental conditions (e.g., sample size, reaction times) of these studies often limit the transferability of findings to field settings. This study was prompted by the limitations identified in the previous studies and the generally limited information on this subject area. A literature search indicates that the following questions are still largely unanswered: (i) How much of applied plant-available Cu will be present at a specific time? (ii) What are the reaction rates and mechanism of Cu fixation in these soils? (iii) How do the findings from i and ii compare to those of other micronutrients? (iv) How would the findings from i, ii, and iii vary among chelated and non-chelated micronutrient compounds in these semiarid soils? Thus, the objectives of this study were to examine and compare the fixation and fixation kinetics of Cu in chelated (ethylene diamine tetraacetic acid, EDTA) and non-chelated mixed systems in the semiarid soils of the SHP, US. Findings from this study could be extended to other semiarid to arid regions of the world facing similar environmental challenges.

2 Materials and methods

2.1 Soil description and sampling

Soil samples were collected from three different crop production sites in west Texas. Sampling was restricted to the depths of 0–15 cm (surface) and 15–30 cm (subsurface) on representative soils from three important agricultural soil series in the SHP, namely the Amarillo (A), Pullman (P), and Mansker (M), for a total of six composite soil samples (Table 1). Soils and sites of interest were identified using the Web Soil Survey (WSS) of the Natural Resources Conservation Service (NRCS). Soil samples were collected using a digging spade marked at 0–15 and 15–30 cm depths. At each field, representative soil samples were collected from approximately 12–15 spots within the field and combined to get a composite sample of about 10 kg of each soil depth. The selected depths are the typical ones commonly examined in most soil fertility and nutrient management studies (Havlin et al., 2013).

2.2 Soil characterization

A subsample of each original (untreated) soil was ground, passed through a 2 mm sieve, and stored in plastic bags at a room temperature of approximately 23 °C. Soil samples were analyzed for a suite of chemical and physical properties. Soil $\mathrm{pH}_{1:2}$ and $\mathrm{EC}_{1:2}$ were determined on a 1 : 2 soil / water ratio using the applicable methods described by Sparks et al. (1996). Soil OM was estimated using the loss on ignition method (at 400 °C and 8 h) following the procedure by Nelson and Sommers (1982). Percentages of $CaCO_3$ were determined using the tensimeter method 4E and 4E1 of the United States Department of Agriculture NRCS-Soil Survey Investigation Report (Soil Survey Staff, 2014). Soil particle size was determined using the modified hydrometer method as described by Gee and Bauder (1986). Plant-available micronutrients (Cu, Fe, Mn, and Zn) were determined using diethylene triamine pentaacetic acid (DTPA) extraction following the procedure by Lindsay and Norvell (1978). Soil test P was determined using the Mehlich 3 procedure (Mehlich, 1984). Total elemental analysis was conducted with the DigiPREP digestion system using USEPA Method 3050B. Concentrations of elements in all extracts were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES; iCAP 7400, Thermo Scientific, Waltham, MA).

Table 1. Soil classification and identification of selected semiarid alkaline soils of the Southern High Plains, USA.

Soil series (classification)	Sample ID	Depth (cm)	Sampling location	pH	EC (dS m^{-1})	OM	$CaCO_3$	Clay (%)	Sand	Silt	Textural class
Amarillo (fine-loamy, mixed, superactive, thermic Aridic Paleustalfs)	A_a	0–15	33.6058° N;	8.07	0.24	1.05	2.41	17.8	74.9	7.40	SL
	A_b	15–30	101.9073° W	8.35	0.22	0.93	5.59	24.0	64.2	11.8	SCL
Mansker (coarse-loamy, carbonatic, thermic Calcidic Paleustolls)	M_a	0–15	34.1261° N;	8.12	0.27	1.63	0.98	27.9	56.5	15.6	SCL
	M_b	15–30	101.5899° W	8.20	0.25	1.24	0.13	41.9	40.9	17.2	C
Pullman (fine, mixed, superactive, thermic Torrertic Paleustolls)	P_a	0–15	34.05901° N;	7.52	0.22	1.56	2.34	32.8	39.9	27.3	CL
	P_b	15–30	101.4773° W	8.02	0.24	1.57	4.16	33.0	38.7	28.3	CL

SCL: sandy clay loam; SL: sandy loam; CL: clay loam; C: clay; EC: electrical conductivity; OM: organic matter.

2.3 Sample preparation and treatment application

Each composite soil sample was thoroughly mixed and a representative portion taken to fill a 4 L plastic pot. Sorghum (*Sorghum bicolor*) was then planted and grown over a period of 35 days in the greenhouse with no nutrients added. This practice was optional and primarily aimed at depleting the original micronutrient level of the soils prior to treatment application. Following this practice, samples were crushed, air dried, thoroughly mixed, ground, and passed through a 2 mm sieve. Two sets of 250 g samples were weighed from each soil. One set was treated with a mixture of chelated (EDTA) micronutrients and the other with a mixture of non-chelated micronutrients, using 80 mL solution of each fertilizer compound's mixture, prepared in order to add 5 mg of each micronutrient (Cu, Mn, Zn, and Fe) to 1 kg of soil. The non-chelated micronutrient compounds used were $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot H_2O$, and $FeSO_4 \cdot 7H_2O$, and the chelated compounds were Cu-EDTA, Mn-EDTA, Zn-EDTA, and Fe-EDTA. There were a total of six soil samples and two sets of micronutrient amendments for a total of 12 soil-fertilizer treatments, each replicated twice. Subsamples were taken from each treated sample at 2, 5, 7, 14, 21, 28, 35, 49, 63, 77, and 90 days after treatment and analyzed for plant-available micronutrients using a DTPA extraction technique (Lindsay and Norvell, 1978). After each subsampling event, the remaining soil samples were wetted with water to approximately field capacity. Within the first 7 days, the soils were wetted after each subsampling; however, after the first 7 days, sampling was conducted at 7–14 days intervals, so the soil samples were watered every 7 days. The periodic wetting of the soil was to simulate the wetting and drying cycle obtainable under field conditions and also provide a medium to facilitate chemical reactions in the soil.

2.4 Extraction procedure

The preparation of DTPA extractant and the extraction procedure followed the method described by Lindsay and Norvell (1978), the most commonly used technique for extracting available micronutrient cations such as Fe, Mn, Cu, and Zn (Liang and Karamanos, 1993). Briefly, 10 g of air-dried soil were placed in a 50 mL plastic tube and 20 mL of DTPA extracting solution was added. The tubes were placed on a reciprocal shaker for 2 h at approximately 25 °C and 180 oscillations per minute. After shaking, samples were centrifuged for 10 min at 4000 rpm, and the resulting solutions were filtered into 16 mm borosilicate glass tubes using Whatman® 2 filter paper. Soil extraction was conducted in duplicate. All filtrates were analyzed for Fe, Cu, Zn, and Mn using ICP-OES (iCAP 7400, Thermo Scientific, Waltham, MA) following USEPA Method 200.7 (USEPA-ICP Users Group, 1982). Instrument calibration was performed using standard reference materials and checked using second source standards from a different vendor. Check samples were inserted after every 20–25 samples. The relative percentage difference between duplicates was also examined and 10 % was set as the acceptance standard.

2.5 Statistical analyses

Statistical analyses were performed using statistical analysis software (SAS 9.4; SAS Institute, Cary, NC, USA). Where applicable, differences among means were examined using PROC GLM, and a mean comparison was conducted using Fisher's Least Significance Difference test at α level of 0.05. The data obtained from the kinetic studies were fitted to selected kinetic models (Table 6) to derive the needed parameters using the PROC NLIN procedure. Single linear regression analyses used in examining changes in available Cu

Table 2. Soil total element analysis of the studied semiarid alkaline soils (in mg kg^{-1}) of the Southern High Plains, USA.

Series	Soil ID	Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	P	Pb	Zn
Amarillo	A_a	17 187	30.9	1823	5.50	11 946	2848	2537	170	1.00	375	41.1	44.5
	A_b	13 823	31.7	4307	5.60	9623	2791	2205	144	0.90	197	34.8	41.6
Mansker	M_a	13 808	35.1	21 008	6.10	9552	3004	2341	135	6.80	186	33.7	51.5
	M_b	16 840	35.1	11 584	7.10	11 856	3554	3103	202	7.00	158	41.5	59.1
Pullman	P_a	11 571	33.8	7252	6.10	8191	2926	2015	128	0.70	196	32.1	42.8
	P_b	12 943	33.7	14 433	6.00	8964	3029	2199	130	0.70	215	33.4	41.6
Mean		14 362	33.4	10 068	6.07	10 022	3025	2400	152	2.85	221	36.1	46.9
Standard deviation		2215	1.74	7073	0.57	1544	274	386	29.1	3.14	77.6	4.12	7.05

with respect to other micronutrients were conducted using the PROC REG procedure.

3 Results and discussions

3.1 Soil characteristics

Selected chemical and physical properties of the studied soils are summarized in Table 1. Average soil pH was 8.05. Soil pH was generally higher in the 15–30 cm depth by 0.08, 0.28, and 0.50 pH units for the Mansker, Amarillo, and Pullman soil series, respectively. The average soil OM content was 1.33 %, falling within a range of 0.93 to 1.57 % among soil depths. These values are typical of the semiarid alkaline soils of the SHP. Average soil EC value was 0.24 dS m^{-1}, falling within a narrow range of 0.22–0.27 dS m^{-1}. The observed soil EC values indicate that these agricultural soils are not salt impacted. Calcium carbonate content varied from 0.13 to 5.59 % among depths and were almost twofold higher in the 15–30 cm depth in the Amarillo and Pullman soils. Average clay contents within the 0–15 and 15–30 cm depths were 26.2 and 32.9 %, respectively, with a difference of 0.24, 6.2, and 14.1 % for Pullman, Amarillo, and Mansker, respectively. Accordingly, the textural classes vary from sandy loam (Amarillo) to clay (Mansker) as presented in Table 1. The soil properties discussed here are typical of those of soils of the semiarid climates (Chesworth, 2008).

The results of the total elemental analysis are presented in Table 2. The concentrations of elements such as Ca, Mg, Na, K, and P in these semiarid soils are typical of those of most agricultural soils (Adriano, 2001; Udeigwe et al., 2009), particularly those not receiving any form of organic amendments. Likewise, the concentrations of heavy metals such as Fe, Cu, Mn, and Zn were within the typical background levels found in most non-polluted agricultural soils (Adriano, 2001; Kabata-Pendias, 2010). No one soil was consistently higher in all the elements measured and there was no consistent trend in the concentration of the elements with depth in each soil series.

The initial background levels of available nutrients are shown in Table 3. Means of the DTPA-extractable Fe, Mn, Cu, and Zn are 5.30, 5.01, 0.81, and 0.38 mg kg^{-1}, respectively. These concentrations indicate an insufficient level of these nutrients and are typical of most semiarid soils (Havlin et al., 2013). Soil test P varied more widely, ranging from 8.93 to 123 mg kg^{-1}, and was generally higher in the top soil, suggesting a possible P input to some of these soils through fertilization.

3.2 Copper fixation pattern (short- and long-term examination)

Percent estimates of fixed Cu determined after the first 14 days (designated as the short term), and 90 days (the long term) are presented in Table 4. The result is presented as the averages for all soils within each depth examined because the examination of individual soils showed no justifiable difference or pattern among the soils that is worth discussing. Comparison was made between the chelated and non-chelated micronutrient treatments. Average values from the three soil series examined revealed that within the non-chelated system, approximately 32 and 39 % of the added Cu was fixed in the 0–15 and 15–30 cm depths, respectively, after the first 14 days. When compared to the chelated system, approximately 13.7 and 14.1 % of the added Cu were fixed in the 0–15 and 15–30 cm depths, respectively. The averages for both depths after the first 14 days were 35.5 and 13.9 % for non-chelated and chelated systems, respectively. These numbers strongly suggest that chelating with EDTA reduced the fixation of Cu by soil constituents (Chiu et al., 2005), rendering Cu more available in these semiarid alkaline soils.

Copper fixation after 90 days (long-term fixation) was also examined. Approximately 48 and 56 % of available Cu was fixed after 90 days in the non-chelated system within the 0–15 and 15–30 cm depths, respectively. These numbers compared to the chelated system were 43.2 and 47.2 % for the 0–15 and 15–30 cm depths, respectively. Average fixations for both depths (all soils) after 90 days were 52.1 % for the non-chelated system and 45.2 % for the chelated system. The

Table 3. Selected plant-available nutrients (in mg kg^{-1}) in the studied semiarid alkaline soils of the Southern High Plains, USA.

Series	Sample ID	Fe_{DTPA}	Mn_{DTPA}	Cu_{DTPA}	Zn_{DTPA}	P_{M3}
Amarillo	$A2_a$	9.73	4.53	0.97	0.96	123
	$A2_b$	3.32	3.25	0.54	0.20	58.7
Mansker	M_a	6.83	5.92	0.99	0.20	33.4
	M_b	3.14	7.09	0.89	0.19	8.93
Pullman	P_a	3.79	4.97	0.59	0.56	28.1
	P_b	4.97	4.29	0.85	0.17	11.6
Mean		5.30	5.01	0.81	0.38	44.0
Standard deviation		2.57	1.34	0.19	0.32	42.7

Abbreviations: DTPA: diethylene triamine pentaacetic acid; M3: Mehlich 3.

Table 4. Average percentage (with standard deviation) of plant-available copper fixed after 14 and 90 days in the non-chelated and chelated systems of the semiarid alkaline soils of the Southern High Plains, USA.

Cu system	Depth (cm)		Percentage fixed after 14 days	90 days
Non-chelated	0–15	($n = 3$)	32.0 (6.0)a	48.4 (12.1)a
	15–30	($n = 3$)	39.1 (9.8)a	55.9 (2.7)a
	All	($n = 6$)	35.5 (2.2)A	52.1 (7.3)A
Chelated	0–15	($n = 3$)	13.7 (9.2)a	43.2 (0.4)a
	15–30	($n = 3$)	14.1 (11.9)a	47.2 (7.4)a
	All	($n = 6$)	13.9 (10.4)B	45.2 (3.5)A

Mean values within a column in a given Cu system with the same lowercase letter and mean values within a column for the Cu systems with the same upper case letter are not statistically different (Fisher's LSD $\alpha = 0.05$).

findings indicated a narrower difference of approximately 7 % between the non-chelated and chelated systems in the long term (90 days) compared to the 22 % observed in the short term (14 days). This could possibly be attributed to the fact that the strength of the chelate decreases with time; thus, more Cu is fixed by other soil constituents over time. The findings here are partly supported by the study of Meers et al. (2005), who estimated a half life of 39 to 59 days for EDTA in doses of 0.8 to 1.6 mmol experimented in a heavy metal phytoextraction study, suggesting that the effectiveness of EDTA on micronutrient mobilization in soil systems will decrease over time. The slightly higher fixation of Cu in the subsurface soil could be partly attributed to its higher clay content. Strong soil-clay–heavy-metal interactions have previously been documented in soils of this region (Udeigwe et al., 2015) and such interactions could reduce the amount of plant-extractable Cu.

3.3 Changes in available Cu with respect to other micronutrients

The changes in the concentration of available Cu over the experimental period of 90 days were compared to those of other micronutrients in the mixture. Relationships within individual soils were examined, but this did not show findings worth focusing the discussion on; thus the findings summarized are averages for the soils at each depth and for both depths combined (Table 5). Regression analyses were used to evaluate the strengths of the relationships and to further examine the gradient of the change between Cu and each of the other micronutrient elements. In each depth, the amount of available Cu positively and significantly changes with each of the other micronutrients, although to varying degrees.

Overall, the strengths of the relationships were higher in the non-chelated systems (R^2: 0.68–0.94) compared to the chelated (R^2: 0.42–0.81). For each of the relationships examined, the slope was generally higher in the non-chelated systems, suggesting that more Cu will be fixed for each unit of the other micronutrients fixed in the non-chelated system. The findings indicate that in each depth, the change in available Cu with respect to change in Zn (Cu–Zn) was higher than those of Cu–Fe, and Cu–Mn in both the non-chelated and chelated systems, as evidenced from the slope of the equations. When both depths were combined for each element, within the non-chelated system, the slopes were 0.40 (Cu–Fe), 0.31 (Cu–Mn), and 1.04 (Cu–Zn), and 0.26 (Cu–Fe), 0.22 (Cu–Mn), and 0.90 (Cu–Zn) for the chelated system. Within the non-chelated system, the findings suggest that a 1 mg kg^{-1} change in the concentration of available Fe, Mn, and Zn, is associated with a 0.40, 0.31, and 1.04 mg kg^{-1} change in available Cu, respectively, in these semiarid alkaline soils of the SHP. The information obtained here has not previously been reported for these soils and provides a good approximation of how Cu changes in respect to other micronutrients in both chelated and non-chelated systems in these semiarid alkaline soils.

Table 5. Changes in available copper with respect to other micronutrient elements (Fe, Mn, and Zn) in the non-chelated and chelated systems of the studied semiarid alkaline soils of the Southern High Plains, USA ($n = 9$).

	Fe		Mn		Zn	
Non-chelated						
0–15	$y = 0.35x - 0.17$	0.91^{b}	$y = 0.25x + 1.95$	0.77^{b}	$y = 0.92x + 0.80$	0.92^{b}
15–30	$y = 0.45x - 0.04$	0.84^{c}	$y = 0.38x + 1.20$	0.68^{b}	$y = 1.14x + 0.95$	0.94^{c}
All	$y = 0.40x - 0.13$	0.90^{c}	$y = 0.31x + 1.59$	0.77^{b}	$y = 1.04x + 0.83$	0.93^{c}
Chelated						
0–15	$y = 0.24x + 1.41$	0.74^{b}	$y = 0.17x + 3.29$	0.52^{a}	$y = 0.86x + 0.87$	0.78^{b}
15–30	$y = 0.27x + 2.45$	0.78^{b}	$y = 0.30x + 2.76$	0.59^{a}	$y = 0.64x + 2.43$	0.42^{a}
All	$y = 0.26x + 1.89$	0.81^{c}	$y = 0.22x + 3.14$	0.56^{a}	$y = 0.90x + 1.05$	0.65^{b}

[a] significant at $\alpha = 0.05$; [b] significant at $\alpha = 0.01$; [c] significant at $\alpha = 0.001$.

Table 6. Kinetic models used for the study of copper fixation in selected semiarid alkaline soils of the Southern High Plains, USA.

Kinetic model	Equation	Parameter
Zero-order	$q_t = q_0 - k_0 t$	k_0, zero-order rate constant ($\mathrm{mg\,kg^{-1}\,d^{-1}}$)
First-order	$\ln q_t = \ln q_0 - k_1 t$	k_1, first-order rate constant ($\mathrm{d^{-1}}$)
Second-order	$1/q_t = 1/q_0 - k_2 t$	k_2, second-order rate constant $(\mathrm{mg\,kg^{-1}})^{-1}$
Power function	$q_t = a_t^b$	a, initial reaction magnitude constant ($\mathrm{mg\,kg^{-1}}\,(\mathrm{h^{-1}})^{b}$) and b, reaction rate constant $(\mathrm{mg\,kg^{-1}})^{-1}$

q_0 and q_t are the amount of micronutrients at time zero and t, respectively.

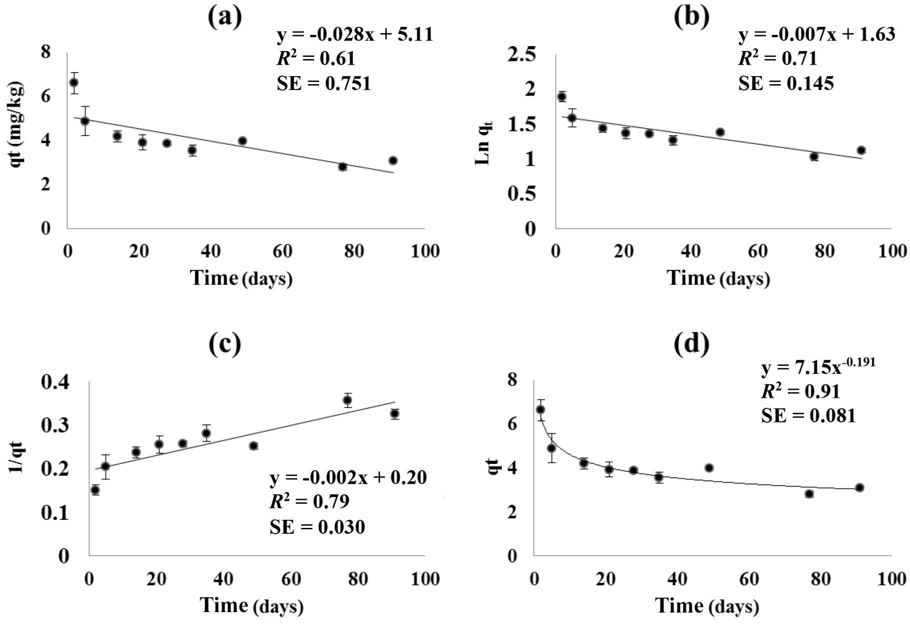

Figure 1. Amount of diethylene triamine pentaacetic acid (DTPA)-extractable copper over the long term (90 days) in the *non-chelated* system fitted to **(a)** zero-order, **(b)** first-order, **(c)** second-order, and **(d)** power function models (q_t denotes the amount remaining at time t ($\mathrm{mg\,kg^{-1}}$); error bars are for standard errors computed from six data points).

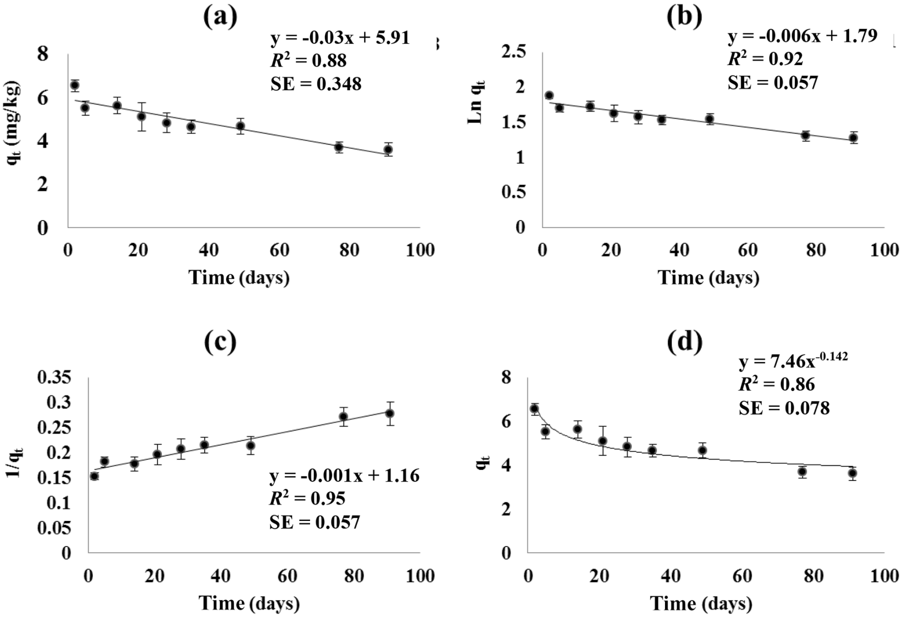

Figure 2. Amount of diethylene triamine pentaacetic acid (DTPA)-extractable copper over the long term (90 days) in the *chelated* system fitted to **(a)** zero-order, **(b)** first-order, **(c)** second-order, and **(d)** power function models (q_t denotes the amount remaining at time t (mg kg^{-1}); error bars are for standard errors computed from six data points).

Table 7. Experimental data from copper kinetic studies fitted to zero-, first-, and second-order models, and power function models.

	Copper system	Depth (cm)		Zero		First		Second		Power	
				R^2	SE	R^2	SE	R^2	SE	R^2	SE
90 days	Non-chelated	0–15	($n = 3$)	0.64	0.705	0.71	0.148	0.75	0.035	0.89	0.091
		15–30	($n = 3$)	0.56	0.828	0.68	0.155	0.77	0.029	0.89	0.083
		All	($n = 6$)	0.61	0.751	0.71	0.145	0.79	0.030	0.91	0.081
	Chelated	0–15	($n = 3$)	0.79	0.477	0.83	0.09	0.85	0.019	0.84	0.087
		15–30	($n = 3$)	0.88	0.337	0.92	0.057	0.94	0.011	0.78	0.095
		All	($n = 6$)	0.88	0.348	0.92	0.057	0.95	0.057	0.86	0.078
35 days	Non-chelated	All	($n = 6$)	0.71	0.671	0.78	0.145	0.85	0.030	0.96	0.081
	Chelated	All	($n = 6$)	0.82	0.327	0.85	0.054	0.87	0.009	0.87	0.049

SE: standard error of regression line.

3.4 Kinetics of copper fixation

Copper fixation in the chelated and non-chelated systems were further examined by fitting the data obtained from kinetic experiments to various kinetic models. A number of kinetic models (Table 6) were examined based on the experimental conditions of this study and evidence gathered from previous studies (Dang et al., 1994; Reyhanitabar and Gilkes, 2010; Rajashekhar Rao, 2015). Coefficient of determination (R^2) and standard error (SE) were employed as criteria for evaluating the best fit among the models examined (Dang et al., 1994; Reyharitabar and Gilkes, 2010). Fixation kinetics were studied within soils and depths. However, the individual examination of soils did not show justifiable reasons to focus the discussion on the comparison among them as earlier intended. Thus, for further examination, average data points for all three soils were used, an approach that also enhanced the statistical evaluations.

Experimental data from kinetic studies were fitted to zero-, first-, and second-order models, as well as to power function models, and findings are summarized in Table 7. In all the models, q_t represents the amount of DTPA-extractable (plant-available) Cu remaining at time t, in days. Close examination reveals a comparable trend between the depths of 0–15 and 15–30 cm and hence there were no findings among

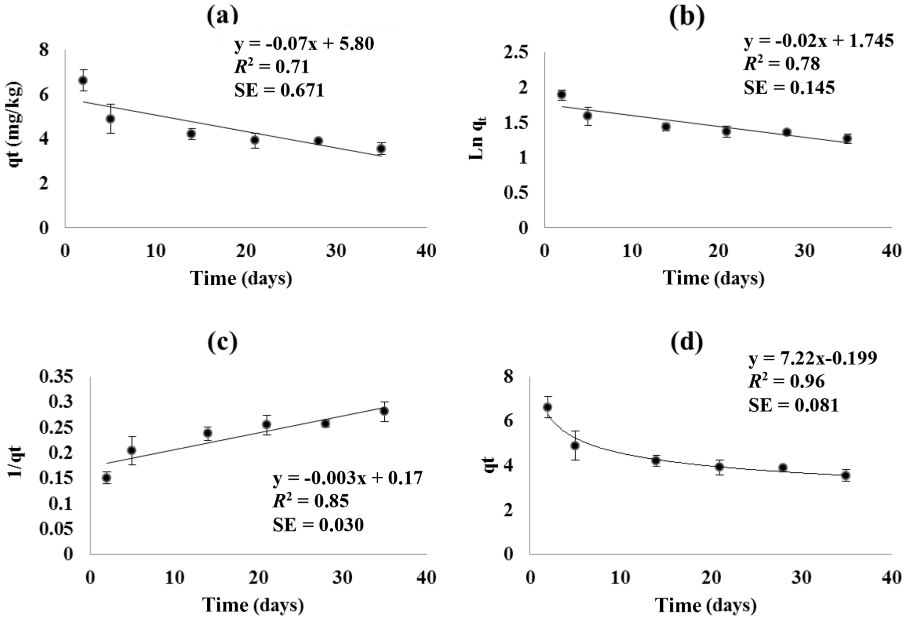

Figure 3. Amount of diethylene triamine pentaacetic acid (DTPA)-extractable copper over the short term (35 days) in the *non-chelated* system fitted to **(a)** zero-order, **(b)** first-order, **(c)** second-order, and **(d)** power function models (q_t denotes the amount remaining at time t ($\mathrm{mg\,kg^{-1}}$); error bars are for standard errors computed from six data points).

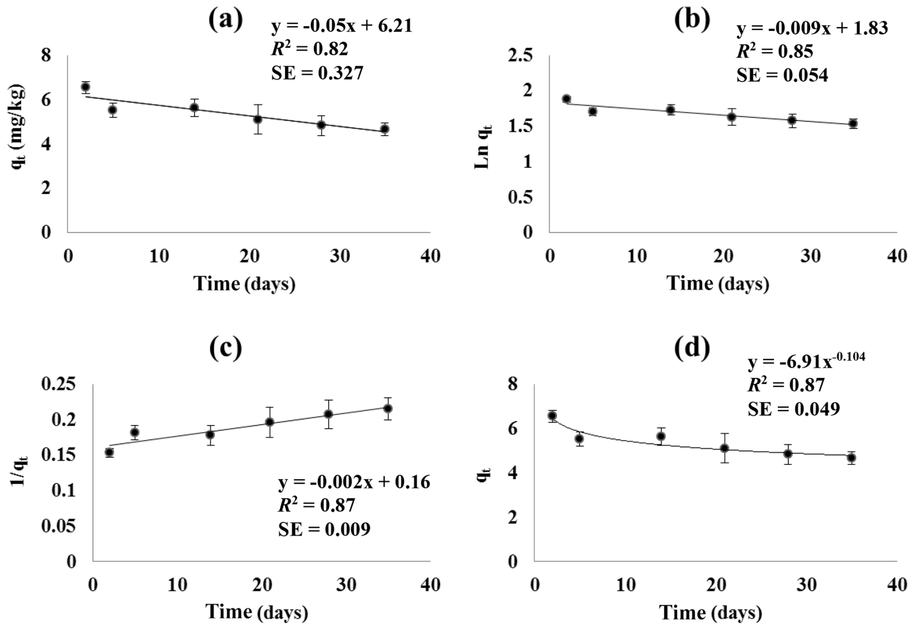

Figure 4. Amount of diethylene triamine pentaacetic acid (DTPA)-extractable copper over the short term (35 days) in the *chelated system* fitted to **(a)** zero-order, **(b)** first-order, **(c)** second-order, and **(d)** power function models (q_t denotes the amount remaining at time t ($\mathrm{mg\,kg^{-1}}$); error bars are for standard errors computed from six data points).

depths worth discussing. As a result, discussions will be concentrated on models derived using the average values of all soils and depths. It was evident that fixation of available Cu was poorly described by the zero-, first-, and second-order models (R^2: 0.61–0.79, SE: 0.030–0.751) but slightly better by the power function model ($R^2 = 0.91$, SE $= 0.081$). A better fit to the power function model suggests that the fixation of plant-available Cu in this mixed system of non-chelated micronutrients is somewhat nonlinear over the 90 days' experimental period (Fig. 1), an indication of a more complex reaction type. This finding was similar to that obtained when Cu was examined in a single system (data not shown). Within the chelated system, the finding was somewhat different (Fig. 2) as Cu fixation was better described by the second-order model ($R^2 = 0.95$, SE $= 0.010$) compared to the other models (R^2: 0.86–0.92). This better fit to the second-order model could imply that the reaction rate depends on the concentration of two reactants (Evangelou, 1998; Sparks, 2003), i.e., Cu and another soil constituents, for e.g., other micronutrients such as Fe, Mn, or Zn. In retrospect, a better fit to the zero-order model implies that the rate of reaction does not depend on the concentration of the reactant (Cu), while a better fit to the first-order model will imply that the rate of reaction is dependent on the concentration of only one reactant (e.g., Cu) (Evangelou, 1998; Sparks, 2003).

Further examination of the data points suggests a possible discontinuity in the slope or pattern of the data distribution before and after day 35, suggesting a likely difference in the mechanisms of Cu fixation before and after the first 35 days. These sets of data points were further separated and examined (Fig. 3 and Table 7). Within the non-chelated system, Cu fixation in the first 35 days was better described by the power function model ($R^2 = 0.96$, SE $= 0.081$) (Fig. 3). When compared to the chelated system, Cu fixation followed the second-order and power function models more closely at about the same degree ($R^2 = 0.87$) (Fig. 4). The findings revealed that the reduction in the amount of available Cu occurred at a slower pace in the chelated system compared to the non-chelated system as evidenced from the reaction rate constants of 0.104 and 0.192 $\mathrm{mg\,kg^{-1}\,day^{-1}}$, respectively.

3.5 Significance of findings to copper management

The adherence of the fixation of non-chelated Cu in the examined semiarid soils to the power function model is an indication of a more complex reaction type when compared to the chelated Cu which followed the second-order model. Findings substantiate the need to apply Cu micronutrient in the chelated form on these semiarid soils as significantly less chelated Cu was fixed, particularly within the first 14 days. Findings further suggest the significance of timing, given that about 68 % of the total Cu fixed was in the first 14 days and that the effectiveness of the chelated compound tended to decrease over time, leading to a narrower difference between chelated and non-chelated compounds. The relationships developed from the examination of the change in available Cu with respect to other micronutrients could be used as predictive tools. The reaction rate constants obtained from this study could be used to approximate how much of added Cu micronutrient will be available at a specific point in time in both chelated and non-chelated systems in these semiarid soils. A very important application of the findings from this study will be for the comparison of the fixation pattern of Cu to those of other micronutrients within these semiarid soils. Reaction rate constants could be compared to those obtained for Cu in other soils. The applications developed from this study provide a basis for a more mechanistic approach to evaluating the effectiveness of commercial micronutrient products and comparisons among products by examining their fixation patterns and kinetic parameters. A database of the reaction rate constants derived for different chelated and non-chelated Cu compounds can be compared among themselves and used as a tool for making a more informed decision on Cu management on these semiarid soils.

4 Conclusions

Kinetic models could be used to further our understanding and examine Cu fixation in soils of the semiarid to arid climates. The reduction of plant-available Cu more closely followed the power function and second-order models in the non-chelated and chelated systems, respectively. The findings substantiate the need for the use of chelated compounds and the importance of timing in Cu management in these semiarid soils. Reaction rate constants obtained from this study could be used for the comparison of the fixation pattern of Cu to those of other micronutrients within these semiarid soils, and for comparisons among soils, and also provide a more mechanistic basis for evaluating the effectiveness of different Cu compounds. Results from this study have much practical significance.

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