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

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Abstract

The relationship between the deficiency of a nutrient in plants and its total concentration in the soil is complex. 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 semi-arid soils of the Southern High Plains, US using findings from Cu extraction studies and kinetic models. Approximately, 22 % more Cu was fixed in the non-chelated system 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 micronutrient over time, highlighting the significance of timing even when chelated micronutrients are applied. 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. Reduction in the amount of available Cu was best described by the power function model (R^2 = 0.91, SE = 0.081) in the non-chelated system and second order model (R^2 = 0.95, 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 semi-arid/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 micronutrient 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,

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organic matter (OM), texture, aeration status, calcium carbonate ($CaCO_3$), iron (Fe) oxides, and interaction with other micronutrients, etc. (Havlin et al., 2013). Plant availability of micronutrient 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 amendment 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 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 elevated soil concentration of other micronutrients such as Zn, Fe, and 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; Lou 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 United States (US) are of the semi-arid climate and are characteristically alkaline in nature. As can be likened to other arid to semi-arid regions of the world (Amuta 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

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productivity (Mehta et al., 2000; Stout, 2001; Allen et al., 2005; Young et al., 2015). Recent observations have also reveal an increasingly more 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 semi-arid 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, etc.) of these studies often limit the transferability of findings to field settings. This study was prompted by the limitations identified in the aforementioned previous studies and the generally limited information on this subject area. 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 these could compare to those of other micronutrients, and (iv) how these vary among chelated and non-chelated micronutrient compounds in these semi-arid soils. Thus, the objectives of this study was 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 semi-arid soils of the SHP, US. Findings from this study could be extended to other semi-arid to arid regions of the world facing similar environmental challenges.

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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) and represented 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 Services (NRCS). Soil sample was collected using a digging spade marked at 0–15 cm and 15–30 cm depths. At each field, representative soil samples were collected from multiple 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 Sample preparation and treatment application

Each composite soil sample was thoroughly mixed and a representative portion taken to fill a 1 gallon pot. Sorghum (*Sorghum bicolor*) was then planted and grown over a period of 5 wk in the greenhouse with no nutrients added. This practice was optional and primarily aimed at depleting the original micronutrient nutrient level of the soils prior to treatment application. Following this practice, samples were crushed and air dried and air-dried samples thoroughly mixed, ground, and sieved through a 2 mm sieve. Two sets of 250 g samples were weighed from each soil. One set 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 compounds mixture prepared to add 5 mg of each micronutrient (Cu, Mn, Zn, and Fe) to 1 kg of soil (Table 2). 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 compound were Cu-EDTA, Mn-EDTA, Zn-EDTA, and

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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 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 1–2 wk intervals, so the soil samples were watered every week. The periodic wetting of the soil was to simulate the wetting and drying cycle obtainable under field condition and also provide a medium to facilitate chemical reactions in the soil.

2.3 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 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 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 inductively coupled plasma-optical emission spectroscopy (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. Relative percentage difference (RPD) between duplicates were also examined and 10 % set as the acceptance standard.

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2.4 Soil characterization

A subsample of each original (untreated) soil was ground, sieved with a 2 mm sieve and stored at room temperature of approximately 23 °C in plastic bags. Soil samples were analyzed for a suite of chemical and physical properties. Soil $pH_{1:2}$ and $EC_{1:2}$ 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 (LOI) method (at 400 °C and 8 h) following the procedure by Nelson and Sommers (1982). Percent $CaCO_3$ was determined using the tensimeter method 4E and 4E1 of the United State Department of Agriculture Natural Resources Conservation Services-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 DTPA extraction following the procedure by Lindsay and Norvell (1978). Soil-test P was determined using Mehlich 3 procedure (Mehlich, 1984). Total elemental analysis was conducted with the DigiPREP Digestion System using USEPA Method 3050B. Concentration of elements in all extracts were measured using ICP-OES (iCAP 7400, Thermo Scientific, Waltham, MA).

2.5 Statistical analyses

Statistical analyses were performed using the Statistical Analysis Software (SAS 9.4, SAS Institute, Cary, NC). Where applicable, differences among means were examined using PROC GLM and mean comparison conducted using Fisher's Least Significance Difference 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 with respect to other micronutrients were conducted using PROC REG procedure.

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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 and 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 semi-arid 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 soil are not salt impacted. The percent $CaCO_3$ varies from 0.13 to 5.59 % among depths and almost two folds higher in the 15–30 cm depth in the Amarillo and Pullman soils. Clay content within the 0–15 cm was lowest in Amarillo (17.8 %) and highest in Mansker (41.9 %), with an average concentration of 26.1 % and was generally higher in the 15–30 cm depth by 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 semi-arid 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 semi-arid 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. Mean of the DTPA-extractable Fe, Mn, Cu, and Zn are 5.18, 5.09, 0.76, and 0.35 $mg\,kg^{-1}$, respectively. These concentrations indicate an insufficient level of these nutrients and

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are typical of those found in semi-arid soils (Havlin et al., 2013). Soil-test P varied more widely, ranging from 8.93 to 123 mg kg^{-1}, and generally higher in the top soil, suggesting a possible P input to some of these soils through fertilization.

3.2 Copper fixation pattern

Percent estimates of fixed Cu determined after the first 14 days (designated as short term), and 90 days (long term) are presented in Table 4. The result is presented as the averages for all soils within each depth examined because examination of individual soils showed no justifiable difference or pattern among the soils that worth focusing our discussions on. 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 were 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 by EDTA reduced the fixation of Cu by soil constituents (Chiu et al., 2005), rendering Cu more available in these semi-arid alkaline soils.

Copper fixation after 90 days (long-term fixation) was also examined. Approximately 48.2 and 56 % of available Cu were 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 non-chelated system and 45.2 % for chelated system. The findings indicated a narrower difference of approximately 7 % between the non-chelated and chelated system on 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 sup-

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ported 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 will decrease over time as a result of biodegradation. 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 was compared to those of other micronutrients in the mixture. Individual soil examination 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 relationship examined, the slope was generally higher in the non-chelated systems, suggesting that more Cu will be fixed with each unit of the other micronutrient 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 0.40, 0.31, and 1.04 mg kg^{-1} change in available Cu re-

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spectively, in these semi-arid alkaline soils of the SHP. The information obtained here is not previously available for these soils and provides a good approximation of how Cu changes with other micronutrients in both chelated and non-chelated systems in these semi-arid alkaline soils.

3.4 Kinetics of copper fixation

The mechanisms of chelated and non-chelated Cu fixation in these soils 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, 2015). Coefficient of determination (R^2) and standard error (SE) were employed as criteria for evaluating 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, second order, and power function models and findings summarized in Table 9. In all the models, qt represents the amount of DTPA extractable (plant-available) Cu remaining at time t, in d. Close examination reveals a comparable trend between the depths of 0–15 and 15–30 cm and hence no findings worth focusing the discussion on depths. 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 fairly better by the power function model (R^2 = 0.91, SE = 0.081). A better fit to the power function model suggest that the fixation of plant-available Cu in this mixed system of non-chelated micronutrients is somewhat not linear over the 90 days experimental period (Fig. 1), an indication of a more complex reaction type This finding was similar to

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those 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 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 slope or pattern of the data distribution before and after day 35, indicating 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 more closely the second order and power function models 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 $mg\,kg^{-1}\,d^{-1}$, respectively.

3.5 Significance of findings to copper management

The adherence of the fixation of non-chelated Cu in the examined semi-arid soils to the power function model is an indication of a more complex reaction mechanism 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 semi-arid soils as significantly less chelated Cu was fixed particularly within the first 14 d. Findings further suggest the significance of timing, given that about 68 % of the total Cu

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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 system in these semi-arid 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 semi-arid 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 semi-arid soils.

4 Conclusions

Kinetic models could be used to further our understanding and examine Cu fixation in soils of the semi-arid 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. Finding substantiate the need for use of chelated compounds and the importance of timing in Cu management in these semi-arid soils. Reaction rate constants obtained from this study could be used for comparison of the fixation pattern of Cu to those of other micronutrients within these semi-arid 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 more practical significance

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because the experiment was designed to ensure the application of findings to field settings, an improvement over most previous studies on micronutrient fixation kinetics.

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Table 1. Soil classification and identification of selected semi-arid 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-Urban (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.

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Table 2. Soil total element analysis of the studied semi-arid alkaline soils of the Southern High Plains, USA.

Series	Soil ID	Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	P	Pb	Zn
		mg kg^{-1}											
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
SD		2215	1.74	7073	0.57	1544	274	386	29.1	3.14	77.6	4.12	7.05

SD = standard deviation.

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Table 3. Selected plant-available nutrients in the studied semi-arid alkaline soils of the Southern High Plains, USA[a].

Series	Sample ID	Fe_{DTPA}	Mn_{DTPA}	Cu_{DTPA}	Zn_{DTPA}	P_{M3}
		mg kg^{-1}				
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
SD		2.57	1.34	0.19	0.32	42.7

[a] = DTPA, diethylene triamine pentaacetic acid; M3 = Mehlich 3.
SD = standard deviation.

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Table 4. Average % (with standard deviation) of plant-available Cu fixed after 14 and 90 days in the non-chelated and chelates systems of the semi-arid alkaline soils of the Southern High Plains, USA[a].

Cu System	Depth[a] cm	% Fixed after 14 days	% Fixed after 90 days
Non-chelated	0–15[c]	32.0 (6.0) a	48.4 (12.1) a
	15–30[c]	39.1 (9.8) a	55.9 (2.7) a
	All[d]	35.5 (2.2) A	52.1 (7.3) A
Chelated	0–15[c]	13.7 (9.2) a	43.2 (0.4) a
	15–30[c]	14.1 (11.9) a	47.2 (7.4) a
	All[d]	13.9 (10.4) B	45.2 (3.5) A

[a] c, $n = 3$; d, $n = 6$. 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 $\alpha = 0.05$).

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Table 5. Changes in available Cu with respect to other micronutrient elements (Fe, Mn, and Zn) in the non-chelated and chelated systems of the studied semi-arid 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 α = 0.05; [b] significant at α = 0.01; [c] significant at α = 0.001.

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Table 6. Kinetic models used for the study of copper fixation in selected semi-arid alkaline soils of the Southern High Plains, USA[a].

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

[a] q_0 and q_t are the amount of micronutrient at time zero and t, respectively.

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

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

[a] SE, standard error of regression line; 0–15 cm, $n = 3$; 15–30 cm, $n = 3$; All, $n = 6$.

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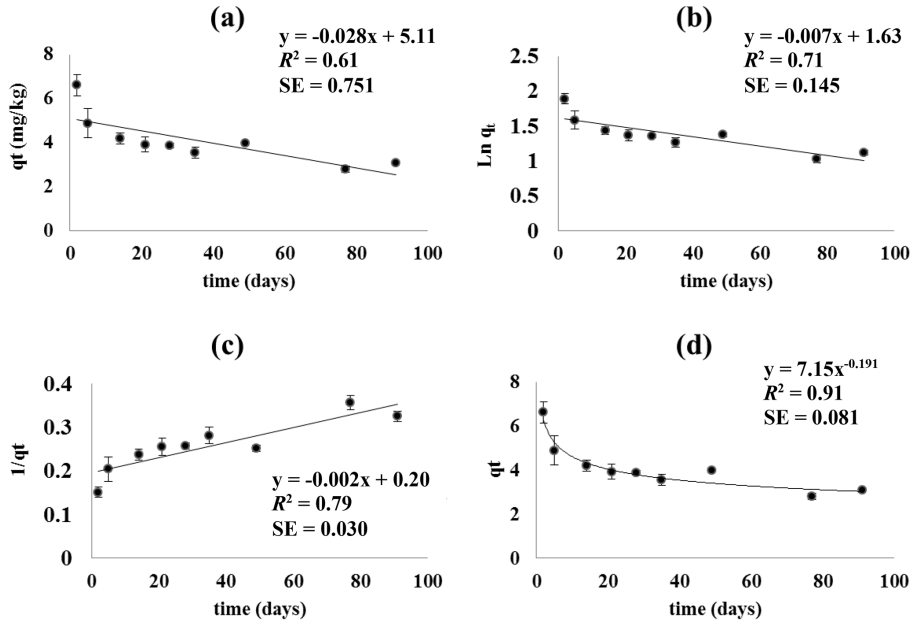

Figure 1. Amount of DTPA-extractable Cu over *long-term* (90 days) from the *non-chelated system* fitted to **(a)** zero order, **(b)** first order, **(c)** second order, and **(d)** power function (q_t = amount remaining at time t, (mg kg^{-1}); error bars are for standard errors computed from 6 data points).

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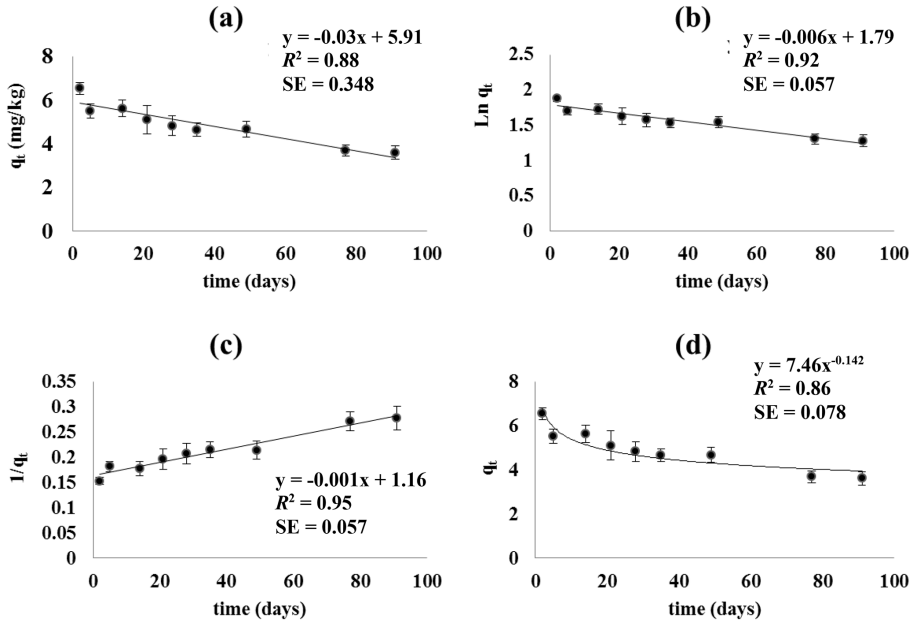

Figure 2. Amount of DTPA-extractable Cu over *long-term* (90 days) from the *chelated system* fitted to **(a)** zero order, **(b)** first order, **(c)** second order, and **(d)** power function models (q_t = amount remaining at time t, (mg kg^{-1}); error bars are for standard errors computed from 6 data points).

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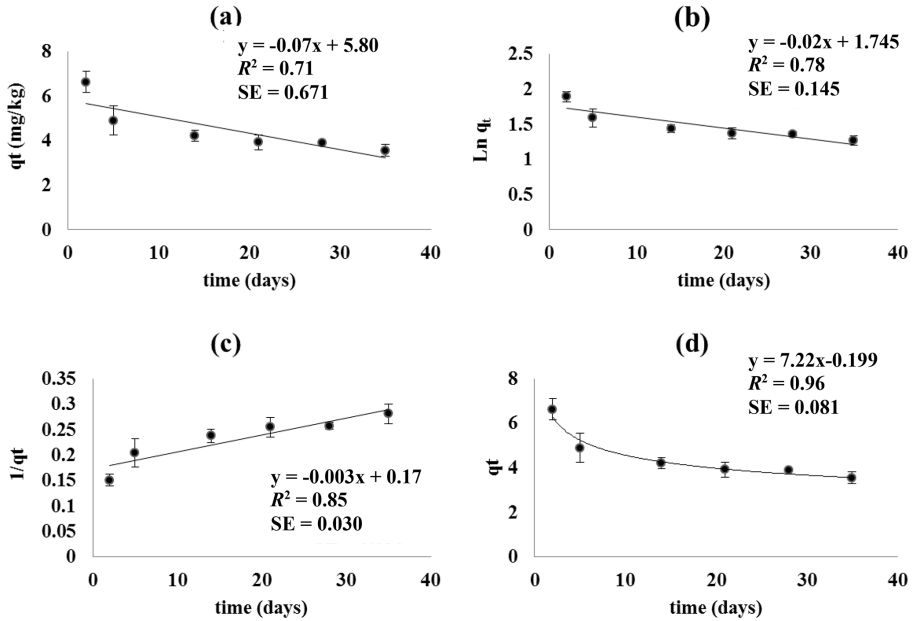

Figure 3. Amount of DTPA-extractable Cu over *short-term* (35 days) from the *non-chelated system* fitted to **(a)** zero order, **(b)** first order, **(c)** second order, and **(d)** power function models (q_t = amount remaining at time t, (mg kg^{-1}); error bars are for standard errors computed from 6 data points).

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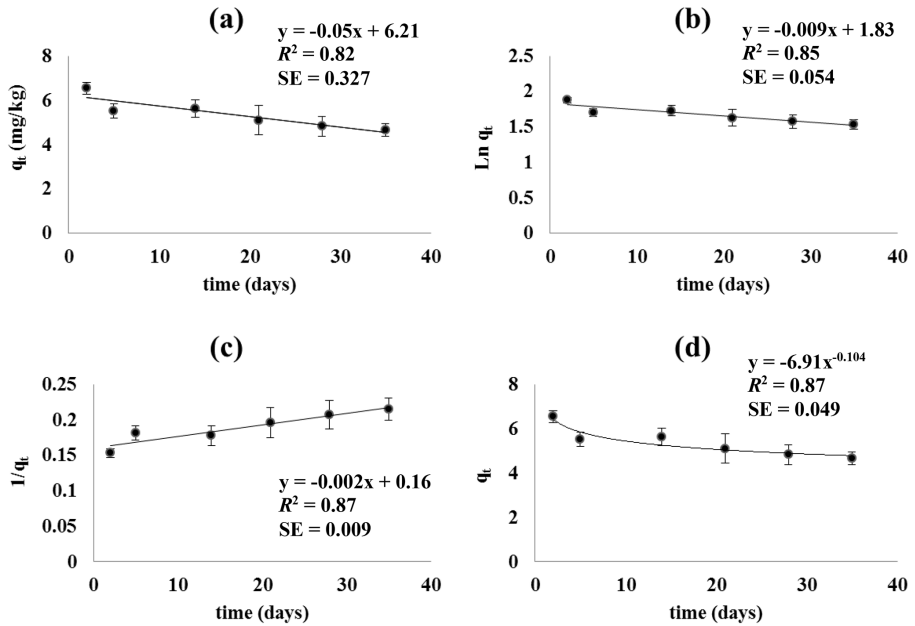

Figure 4. Amount of DTPA-extractable Cu over *short-term* (35 days) from the *chelated system* fitted to **(a)** zero order, **(b)** first order, **(c)** second order, and **(d)** power function models (q_t = amount remaining at time t, (mg kg^{-1}); error bars are for standard errors computed from 6 data points).

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