

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

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26 **Abstract**

27 The relationship between the deficiency of a nutrient in plants and its total
28 concentration in the soil is complex. This study examined and compared the fixation and
29 fixation kinetics of copper (Cu) in chelated (Ethylene diamine tetraacetic acid, EDTA) and
30 non-chelated mixed systems of micronutrients in the semi-arid soils of the Southern High
31 Plains, US using findings from Cu extraction studies and kinetic models. Approximately, 22%
32 more Cu was fixed in the non-chelated system within the first 14 d with only 7% difference
33 between the two systems by day 90. Findings suggest a decrease in the effectiveness of
34 chelated micronutrient over time, highlighting the significance of timing even when chelated
35 micronutrients are applied. The strengths of the relationship of change in available Cu with
36 respect to other micronutrients [iron (Fe), manganese (Mn), and zinc (Zn)] were higher in the
37 non-chelated system (R^2 : 0.68-0.94), compared to the chelated (R^2 : 0.42-0.81) with slopes of
38 0.40 (Cu-Fe), 0.31 (Cu-Mn), and 1.04 (Cu-Zn) in the non-chelated system and 0.26 (Cu-Fe),
39 0.22 (Cu-Mn), and 0.90 (Cu-Zn) in the chelated. Reduction in the amount of available Cu was
40 best described by the power function model ($R^2 = 0.91$, SE = 0.081) in the non-chelated
41 system and second order model ($R^2 = 0.95$, SE = 0.010) in the chelated system. The
42 applications generated from this study could be used as tools for improved micronutrient
43 management and also provide baseline data for future work in other semi-arid/arid alkaline
44 soils of the world. Findings are also more applicable to field settings, an improvement over
45 related previous studies.

46 **Keywords:** Ethylene diamine tetraacetic acid, Southern High Plains, soil fertility, power
47 function model, diethylene triamine pentaacetic acid

48 **1 Introduction**



49
50 Malnutrition resulting from lack of adequate micronutrient in foods, a situation that
51 could be partly attributed to the ease of micronutrient fixation in soil systems, contributes
52 significantly to the global burden of disease (WHO, 2000). The fate of the plant-available
53 portion of micronutrients is controlled by a number of soil factors including soil pH, organic
54 matter (OM), texture, aeration status, calcium carbonate (CaCO_3), iron (Fe) oxides, and
55 interaction with other micronutrients, etc. (Havlin et al., 2013). Plant availability of
56 micronutrient could be a bigger challenge in calcareous or alkaline soils due to their high pH
57 (Rashid and Ryan, 2004; Alloway, 2008). High soil pH leads to decreased solubility and
58 increased fixation of most micronutrients such as copper (Cu), zinc (Zn), Fe, and manganese
59 (Mn) in such soils, leading to reduction in the plant-available portion (Sparks, 2003; Havlin et
60 al., 2013). For Cu, apart from pH, reduction in availability resulting from its interaction with
61 OM functional groups, particularly in soils treated with organic amendment such as animal
62 manure and biosolids, has also been well documented (De Schamphelaere et al., 2004; Pinto
63 et al., 2004). Its availability has also been reported to increase with soil OM (under moderate
64 OM level) and clay content, and to decrease with increase in pH and CaCO_3 (Alloway, 2008).
65 Interactions among nutrients resulting in antagonism are also common (Dimkpa, et al., 2013;
66 Havlin et al., 2013; Bindraban et al., 2015), for instance, plant uptake of Cu is shown to be
67 reduced by elevated soil concentration of other micronutrients such as Zn, Fe, and phosphorus
68 (P) (Havlin et al., 2013).

69 Given the aforementioned challenges, to increase the availability of micronutrients
70 such as Cu to plants, they are preferably applied in the form of synthetic and organic chelates.

71 The advantages of the chelated forms have also been documented under certain soil types and
72 conditions by a number of researchers (Kayser et al., 2000; Sekhon, 2003; Lou et al., 2005;
73 Chiu et al., 2005). However, the heterogeneous nature of soil limits the extension of findings
74 from one soil type to another among regions, thus, often necessitating site-specific studies.

75 The soils of the Southern High Plains (SHP) of the United States (US) are of the semi-
76 arid climate and are characteristically alkaline in nature. As can be likened to other arid to
77 semi-arid regions of the world (Amuta, et al., 2014; Sarah and Zonana, 2015; Torres et al.,
78 2015; Barbero-Sierra et al., 2015; Mureithi et al., 2015), this region (the SHP) is currently
79 facing complex environmental challenges such as drought, declining groundwater quality,
80 wind erosion, and soil salinization that limit agricultural productivity (Mehta et al., 2000;
81 Stout, 2001; Allen et al., 2005; Young et al., 2015). Recent observations have also reveal an
82 increasingly more cases of micronutrient deficiency, which could be attributed to the
83 characteristically high pH soils prevalent in this region and intensive crop production
84 activities. Unfortunately, little to no information is available on the chemistry of
85 micronutrients in the semi-arid alkaline soils of this region, despite the agronomic
86 significance of these soils. Understanding the kinetics of plant-available micronutrient
87 fixation in these soils is vital for developing improved nutrient management plans for
88 agricultural and environmental sustainability. Kinetic parameters obtained can be used for
89 comparisons among micronutrients and among soils. A systematic approach to examining the
90 chemistry of micronutrients in soil systems will encompass the examination of the chemistry
91 of these micronutrients in a mixed system (of a number of other micronutrients).

92 Although a number of studies have examined the kinetics of micronutrient fixation in

93 soils (Manouchehri et al., 2006; Reyhanitabar and Gilkes, 2010; Abbas and Salem, 2011), the
94 experimental conditions (e.g. sample size, reaction times, etc.) of these studies often limit the
95 transferability of findings to field settings. This study was prompted by the limitations
96 identified in the aforementioned previous studies and the generally limited information on this
97 subject area. Literature search indicates that the following questions are still largely
98 unanswered: (i) how much of applied plant-available Cu will be present at a specific time, (ii)
99 what are the reaction rates and mechanism of Cu fixation in these soils, (iii) how these could
100 compare to those of other micronutrients, and (iv) how these vary among chelated and non-
101 chelated micronutrient compounds in these semi-arid soils. Thus, the objectives of this study
102 was to examine and compare the fixation and fixation kinetics of Cu in chelated (Ethylene
103 diamine tetraacetic acid, EDTA) and non-chelated mixed systems in the semi-arid soils of the
104 SHP, US. Findings from this study could be extended to other semi-arid to arid regions of the
105 world facing similar environmental challenges.

106 **2 Materials and Methods**

107 **2.1 Soil description and sampling**

108 Soil samples were collected from three different crop production sites in West Texas.
109 Sampling was restricted to the depths of 0-15 cm (surface) and 15-30 cm (subsurface) and
110 represented soils from three important agricultural soil series in the SHP, namely the Amarillo
111 (A), Pullman (P), and Mansker (M) for a total of six composite soil samples (Table 1). Soils
112 and sites of interest were identified using the Web Soil Survey (WSS) of the Natural
113 Resources Conservation Services (NRCS). Soil sample was collected using a digging spade
114 marked at 0-15 cm and 15-30 cm depths. At each field, representative soil samples were

115 collected from multiple spots within the field and combined to get a composite sample of
116 about 10 kg of each soil depth. The selected depths are the typical ones commonly examined
117 in most soil fertility and nutrient management studies (Havlin et al., 2013).

118 **2.2 Sample preparation and treatment application**

119 Each composite soil sample was thoroughly mixed and a representative portion taken
120 to fill a 1-gallon pot. Sorghum (*Sorghum bicolor*) was then planted and grown over a period
121 of 5 wk in the greenhouse with no nutrients added. This practice was optional and primarily
122 aimed at depleting the original micronutrient nutrient level of the soils prior to treatment
123 application. Following this practice, samples were crushed and air dried and air-dried
124 samples thoroughly mixed, ground, and sieved through a 2-mm sieve. Two sets of 250 g
125 samples were weighed from each soil. One set treated with a mixture of chelated (EDTA)
126 micronutrients and the other with a mixture of non-chelated micronutrients, using 80 ml
127 solution of each fertilizer compounds mixture prepared to add 5 mg of each micronutrient
128 (Cu, Mn, Zn, and Fe) to 1 kg of soil (Table 2). The non-chelated micronutrient compounds
129 used were $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ and the chelated
130 compound were Cu-EDTA, Mn-EDTA, Zn-EDTA, and Fe-EDTA. There were a total of six
131 soil samples and two sets of micronutrient amendments for a total of 12 soil-fertilizer
132 treatments, each replicated twice. Subsamples were taken from each treated sample at 2, 5, 7,
133 14, 21, 28, 35, 49, 63, 77, and 90 d after treatment and analyzed for plant available-
134 micronutrients using DTPA extraction technique (Lindsay and Norvell, 1978). After each
135 subsampling event, the remaining soil samples were wetted with water to approximately field
136 capacity. Within the first 7 d, the soils were wetted after each subsampling, however, after

137 the first 7 d, sampling was conducted at 1-2 wk intervals, so the soil samples were watered
138 every week. The periodic wetting of the soil was to simulate the wetting and drying cycle
139 obtainable under field condition and also provide a medium to facilitate chemical reactions in
140 the soil.

141 **2.3 Extraction procedure**

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

157 **2.4 Soil characterization**

158 A subsample of each original (untreated) soil was ground, sieved with a 2-mm sieve

159 and stored at room temperature of approximately 23°C in plastic bags. Soil samples were
160 analyzed for a suite of chemical and physical properties. Soil pH_{1:2} and EC_{1:2} were determined
161 on a 1:2 soil/water ratio using the applicable methods described by Sparks et al. (1996). Soil
162 OM was estimated using the loss on ignition (LOI) method (at 400°C and 8 h) following the
163 procedure by Nelson and Sommers (1996). Percent CaCO₃ was determined using the
164 tensimeter method 4E and 4E1 of the United State Department of Agriculture Natural
165 Resources Conservation Services-Soil Survey Investigation Report (Soil Survey Staff, 2014).
166 Soil particle size was determined using the modified hydrometer method as described by Gee
167 and Bauder (1986). Plant-available micronutrients (Cu, Fe, Mn, and Zn) were determined
168 using DTPA extraction following the procedure by Lindsay and Norvell (1978). Soil-test P
169 was determined using Mehlich 3 procedure (Mehlich, 1984). Total elemental analysis was
170 conducted with the DigiPREP Digestion System using USEPA Method 3050B. Concentration
171 of elements in all extracts were measured using ICP-OES (iCAP 7400, Thermo Scientific,
172 Waltham, MA).

173 **2.5 Statistical analyses**

174 Statistical analyses were performed using the Statistical Analysis Software (SAS 9.4,
175 SAS Institute, Cary, NC). Where applicable, differences among means were examined using
176 PROC GLM and mean comparison conducted using Fisher's Least Significance Difference at
177 α level of 0.05. The data obtained from the kinetic studies were fitted to selected kinetic
178 models (Table 6) to derive the needed parameters using the PROC NLIN procedure. Single
179 linear regression analyses used in examining changes in available Cu with respect to other
180 micronutrients were conducted using PROC REG procedure.

181 **3 Results and discussions**

182 **3.1 Soil characteristics**

183

184 Selected chemical and physical properties of the studied soils are summarized in Table

185 1. Average soil pH was 8.05 and was generally higher in the 15-30 cm depth by 0.08, 0.28,
186 and 0.50 pH units for the Mansker, Amarillo, and Pullman soil series, respectively. The
187 average soil OM content was 1.33%, falling within a range of 0.93 to 1.57% among soil
188 depths. These values are typical of the semi-arid alkaline soils of the SHP. Average soil EC
189 value was 0.24 dS m⁻¹ falling within a narrow range of 0.22-0.27 dS m⁻¹. The observed soil EC
190 values indicate that these agricultural soil are not salt impacted. The percent CaCO₃ varies
191 from 0.13 to 5.59% among depths and almost two folds higher in the 15-30 cm depth in the
192 Amarillo and Pullman soils. Clay content within the 0-15 cm was lowest in Amarillo (17.8 %)
193 and highest in Mansker (41.9 %), with an average concentration of 26.1% and was generally
194 higher in the 15-30 cm depth by 0.24, 6.2, and 14.1 % for Pullman, Amarillo, and Mansker,
195 respectively. Accordingly, the textural classes vary from sandy loam (Amarillo) to clay
196 (Mansker) as presented in Table 1. The soil properties discussed here are typical of those of
197 soils of the semi-arid climates (Chesworth, 2008).

198 The results of the total elemental analysis are presented in Table 2. The concentrations
199 of elements such as Ca, Mg, Na, K, and P in these semi-arid soils are typical of those of most
200 agricultural soils (Adriano, 2001; Udeigwe et al., 2009), particularly those not receiving any
201 form of organic amendments. Likewise, the concentrations of heavy metals such as Fe, Cu,
202 Mn, and Zn were within the typical background levels found in most non-polluted agricultural
203 soils (Adriano, 2001; Kabata-Pendias, 2010). No one soil was consistently higher in all the

204 elements measured and there was no consistent trend in the concentration of the elements with
205 depth in each soil series.

206 The initial background levels of available nutrients are shown in Table 3. Mean of the
207 DTPA-extractable Fe, Mn, Cu, and Zn are 5.18, 5.09, 0.76, and 0.35 mg kg⁻¹, respectively.
208 These concentrations indicate an insufficient level of these nutrients and are typical of those
209 found in semi-arid soils (Havlin et al., 2013). Soil-test P varied more widely, ranging from
210 8.93 to 123 mg kg⁻¹, and generally higher in the top soil, suggesting a possible P input to
211 some of these soils through fertilization.

212 **3.2 Copper fixation pattern**

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

226 Copper fixation after 90 d (long-term fixation) was also examined. Approximately
227 48.2% and 56% of available Cu were fixed after 90 d in the non-chelated system within the 0-
228 15 and 15-30 cm depths, respectively. These numbers compared to the chelated system were
229 43.2 % and 47.2% for the 0-15 and 15-30 cm depths, respectively. Average fixations for both
230 depths (all soils) after 90 d were 52.1% for non-chelated system and 45.2% for chelated
231 system. The findings indicated a narrower difference of approximately
232 7% between the non-chelated and chelated system on the long term (90 d) compared to the
233 22% observed in the short term (14 d). This could possibly be attributed to the fact that the
234 strength of the chelate decreases with time, thus, more Cu is fixed by other soil constituents
235 over time. The findings here are partly supported by the study of Meers et al. (2005), who
236 estimated a half-life of 39 to 59 d for EDTA in doses of 0.8 to 1.6 mmol experimented in a
237 heavy metal phytoextraction study, suggesting that the effectiveness of EDTA on
238 micronutrient mobilization will decrease over time as a result of biodegradation. The slightly
239 higher fixation of Cu in the subsurface soil could be partly attributed to its higher clay
240 content. Strong soil clay-heavy metal interactions have previously been documented in soils
241 of this region (Udeigwe et al., 2015) and such interactions could reduce the amount of plant-
242 extractable Cu.

243 **3.3 Changes in available Cu with respect to other micronutrients**

244 The changes in the concentration of available Cu over the experimental period of 90 d
245 was compared to those of other micronutrients in the mixture. Individual soil examination did
246 not show findings worth focusing the discussion on, thus the findings summarized are
247 averages for the soils at each depth and for both depths combined (Table 5). Regression

248 analyses were used to evaluate the strengths of the relationships and to further examine the
249 gradient of the change between Cu and each of the other micronutrient elements. In each
250 depth, the amount of available Cu positively and significantly changes with each of the other
251 micronutrients, although to varying degrees. Overall, the strengths of the relationships were
252 higher in the non-chelated systems (R^2 : 0.68-0.94) compared to the chelated (R^2 : 0.42-0.81).
253 For each of the relationship examined, the slope was generally higher in the non-chelated
254 systems, suggesting that more Cu will be fixed with each unit of the other micronutrient fixed
255 in the non-chelated system. The findings indicate that in each depth, the change in available
256 Cu with respect to change in Zn (Cu-Zn) was higher than those of Cu-Fe, and Cu-Mn in both
257 the non-chelated and chelated systems as evidenced from the slope of the equations. When
258 both depths were combined for each element, within the non-chelated system, the slopes were
259 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
260 (Cu-Zn) for the chelated system. Within the non-chelated system, the findings suggest that a 1
261 mg kg⁻¹ change in the concentration of available Fe, Mn, and Zn, is associated with 0.40,
262 0.31, and 1.04 mg kg⁻¹ change in available Cu respectively, in these semi-arid alkaline soils of
263 the SHP. The information obtained here is not previously available for these soils and
264 provides a good approximation of how Cu changes with other micronutrients in both chelated
265 and non-chelated systems in these semi-arid alkaline soils.

266 **3.4 Kinetics of copper fixation**

267 The mechanisms of chelated and non-chelated Cu fixation in these soils were further
268 examined by fitting the data obtained from kinetic experiments to various kinetic models. A
269 number of kinetic models (Table 6) were examined based on the experimental conditions of

270 this study and evidence gathered from previous studies (Dang et al., 1994; Reyhanitabar and
271 Gilkes, 2010; Rajashekhar, 2015). Coefficient of determination (R^2) and standard error (SE)
272 were employed as criteria for evaluating best fit among the models examined (Dang et al.,
273 1994; Reyharitabar and Gilkes, 2010). Fixation kinetics were studied within soils and depths.
274 However, the individual examination of soils did not show justifiable reasons to focus the
275 discussion on the comparison among them as earlier intended. Thus, for further examination,
276 average data points for all three soils were used, an approach that also enhanced the statistical
277 evaluations.

278 Experimental data from kinetic studies were fitted to zero, first, second order, and
279 power function models and findings summarized in Table 9 . In all the models, qt represents
280 the amount of DTPA extractable (plant-available) Cu remaining at time t , in d. Close
281 examination reveals a comparable trend between the depths of 0-15 and 15-30 cm and hence
282 no findings worth focusing the discussion on depths. As a result, discussions will be
283 concentrated on models derived using the average values of all soils and depths. It was
284 evident that fixation of available Cu was poorly described by the zero, first, and second order
285 models (R^2 : 0.61 - 0.79, SE: 0.030-0.751) but fairly better by the power function model ($R^2 =$
286 0.91, SE = 0.081). A better fit to the power function model suggest that the fixation of plant-
287 available Cu in this mixed system of non-chelated micronutrients is somewhat not linear over
288 the 90-d experimental period (Figure 1), an indication of a more complex reaction type This
289 finding was similar to those obtained when Cu was examined in a single system (data not
290 shown). Within the chelated system, the finding was somewhat different (Figure 2) as Cu
291 fixation was better described by the second order model ($R^2 = 0.95$, SE = 0.010) compared to



292 the other models (R^2 : 0.86 - 0.92). This better fit to the second order model could imply that
293 the reaction rate depends on the concentration of two reactants (Evangelou, 1998; Sparks,
294 2003), i.e., Cu and another soil constituents, for e.g., other micronutrients such as Fe, Mn, or
295 Zn. In retrospect, a better fit to the zero order model implies that the rate of reaction does not
296 depend on the concentration of the reactant (Cu), while a better fit to the first order will imply
297 that the rate of reaction is dependent on the concentration of only one reactant (e.g., Cu)
298 (Evangelou 1998; Sparks 2003).

299 Further examination of the data points suggests a possible discontinuity in slope or
300 pattern of the data distribution before and after day 35, indicating a likely difference in the
301 mechanisms of Cu fixation before and after the first 35 d. These sets of data points were
302 further separated and examined (Figure 3 and Table 7). Within the non-chelated system, Cu
303 fixation in the first 35 d was better described by the power function model ($R^2 = 0.96$, SE =
304 0.081) (Figure 3). When compared to the chelated system, Cu fixation followed more closely
305 the second order and power function models at about the same degree ($R^2 = 0.87$) (Figure 4).
306 The findings revealed that the reduction in the amount of available Cu occurred at a slower
307 pace in the chelated system compared to the non-chelated system as evidenced from the
308 reaction rate constants of 0.104 and 0.192 mg kg⁻¹ d⁻¹, respectively.

309 **3.5 Significance of findings to copper management**

310 The adherence of the fixation of non-chelated Cu in the examined semi-arid soils to
311 the power function model is an indication of a more complex reaction mechanism when
312 compared to the chelated Cu which followed the second order model. Findings substantiate
313 the need to apply Cu micronutrient in the chelated form on these semi-arid soils as

314 significantly less chelated Cu was fixed particularly within the first 14 d. Findings further
315 suggest the significance of timing, given that about 68% of the total Cu fixed was in the first
316 14 d and that the effectiveness of the chelated compound tended to decrease over time leading
317 to a narrower difference between chelated and non-chelated compounds. The relationships
318 developed from the examination of the change in available Cu with respect to other
319 micronutrients could be used as predictive tools. The reaction rate constants obtained from
320 this study could be used to approximate how much of added Cu micronutrient will be
321 available at a specific point in time in both chelated and non-chelated system in these semi-
322 arid soils A very important application of the findings from this study will be for the
323 comparison of the fixation pattern of Cu to those of other micronutrients within these semi-
324 arid soils. Reaction rate constants could be compared to those obtained for Cu in other soils.
325 The applications developed from this study provide a basis for a more mechanistic approach
326 to evaluating the effectiveness of commercial micronutrient products and comparisons among
327 products by examining their fixation patterns and kinetic parameters. A database of the
328 reaction rate constants derived for different chelated and non-chelated Cu compounds can be
329 compared among themselves and used as a tool for making a more informed decision on Cu
330 management on these semi-arid soils.

331 **4 Conclusions**

332 Kinetic models could be used to further our understanding and examine Cu fixation in
333 soils of the semi-arid to arid climates. The reduction of plant available Cu more closely
334 followed the power function and second order models in the non-chelated and chelated
335 systems, respectively. Finding substantiate the need for use of chelated compounds and the

336 importance of timing in Cu management in these semi-arid soils. Reaction rate constants
337 obtained from this study could be used for comparison of the fixation pattern of Cu to those of
338 other micronutrients within these semi-arid soils, and for comparisons among soils, and also
339 provide a more mechanistic basis for evaluating the effectiveness of different Cu compounds.
340 Results from this study have more practical significance because the experiment was designed
341 to ensure the application of findings to field settings, an improvement over most previous
342 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	N 33.6058°;	8.07	0.24	1.05	2.41	17.8	74.9	7.40	SL
	A _b	15-30	W 101.9073°	8.35	0.22	0.93	5.59	24.0	64.2	11.8	SCL
Mansker (Coarse-loamy, carbonatic, thermic Calcic Paleustolls)	M _a	0-15	N 34.1261°;	8.12	0.27	1.63	0.98	27.9	56.5	15.6	SCL
	M _b	15-30	W 101.5899°	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	N 34.05901°;	7.52	0.22	1.56	2.34	32.8	39.9	27.3	CL
	P _b	15-30	W 101.4773°	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

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

Series	Soil ID	-----mg kg ⁻¹ -----											
		Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	P	Pb	Zn
Amarillo	A _a	17187	30.9	1823	5.50	11946	2848	2537	170	1.00	375	41.1	44.5
	A _b	13823	31.7	4307	5.60	9623	2791	2205	144	0.90	197	34.8	41.6
Mansker	M _a	13808	35.1	21008	6.10	9552	3004	2341	135	6.80	186	33.7	51.5
	M _b	16840	35.1	11584	7.10	11856	3554	3103	202	7.00	158	41.5	59.1
Pullman	P _a	11571	33.8	7252	6.10	8191	2926	2015	128	0.70	196	32.1	42.8
	P _b	12943	33.7	14433	6.00	8964	3029	2199	130	0.70	215	33.4	41.6
Mean		14362	33.4	10068	6.07	10022	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

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

Series	Sample ID	F _{DTPA}	M _{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

^aDTPA, diethylene triamine pentaacetic acid; M3, Mehlich 3
SD; Standard Deviation

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* cm	% Fixed after	
		14 days	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

^ac, 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 $\alpha = 0.05$).

1 **Table 5:** Changes in available Cu with respect to other micronutrient elements (Fe, Mn, and Zn) in the non-chelated and chelated
 2 systems of the studied semi-arid alkaline soils of the Southern High Plains, USA (n = 9).

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

* significant at $\alpha = 0.05$; ** significant at $\alpha = 0.01$; *** significant at $\alpha = 0.001$

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18 **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 ($\text{mg} \cdot \text{kg}^{-1} \text{d}^{-1}$)
First order	$\text{Ln } q_t = \text{Ln } q_0 - k_1 t$	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 ($\text{mg} \cdot \text{kg}^{-1}$) ⁻¹
Power function	$q_t = at^b$	a, initial reaction magnitude constant [$(\text{mg} \cdot \text{kg}^{-1}(\text{h}^{-1})^b)$ and b, reaction rate constant ($\text{mg} \cdot \text{kg}^{-1}$) ⁻¹

^a q_0 and q_t are the amount of micronutrient at time zero and t, respectively

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38 **Table 7:** Experimental data from copper kinetic studies fitted to zero, first, second order, and power function models^a.

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	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	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

^aSE, standard error of regression line; 0-15 cm, n = 3; 15-30 cm, n = 3; All, n = 6

67 **Figure Caption**

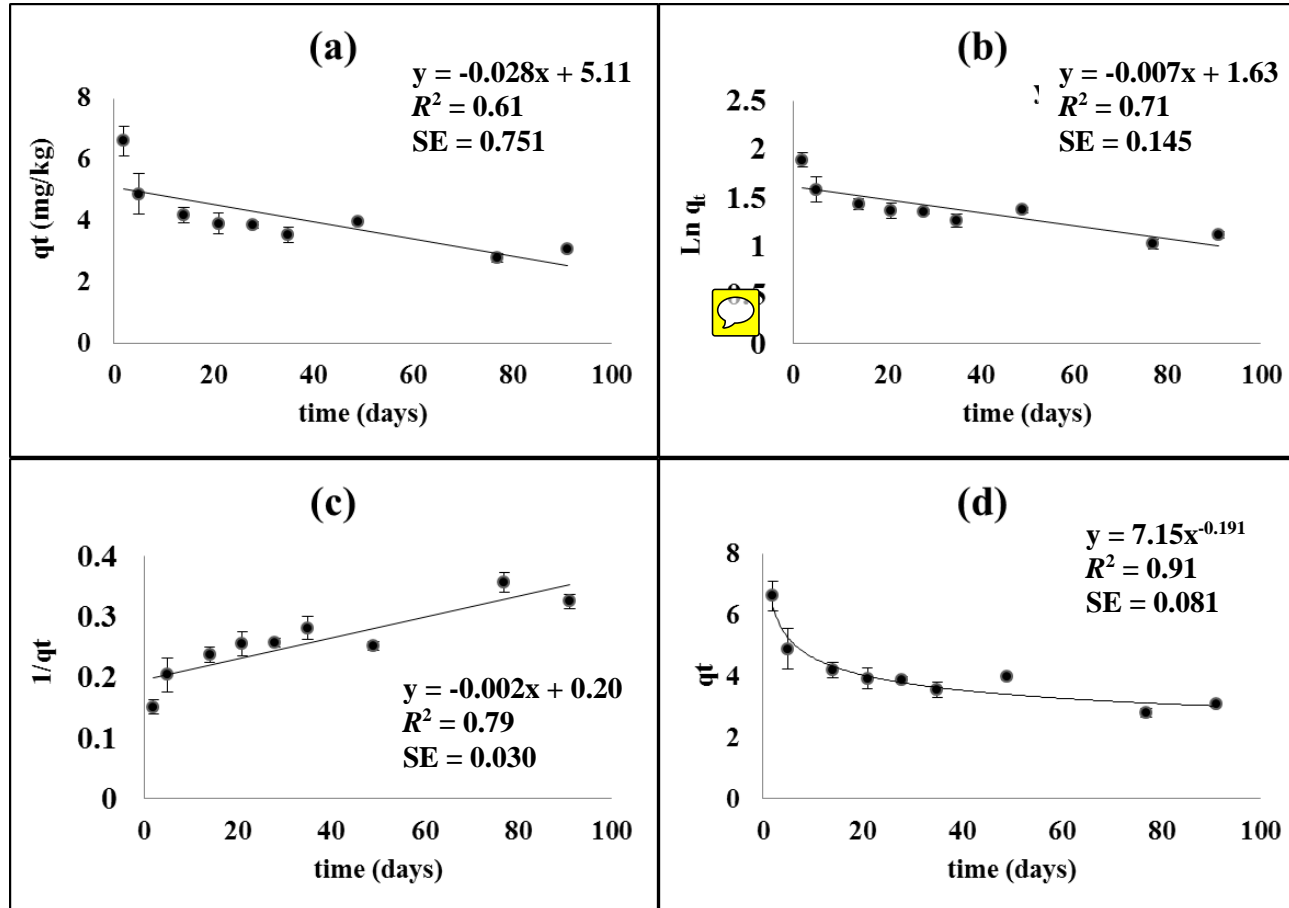
68 **Figure 1:** Amount of DTPA-extractable Cu over *long-term* (90 days) from the *non-chelated*
69 *system* fitted to (a) zero order, (b) first order, (c) second order, and (d) power function ($q_t =$
70 amount remaining at time t, [$\text{mg}\cdot\text{kg}^{-1}$]; error bars are for standard errors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

72 **Figure 2:** Amount of DTPA-extractable Cu over *long-term* (90 days) from the *chelated*
73 *system* fitted to (a) zero order, (b) first order, (c) second order, and (d) power function models
74 ($q_t =$ amount remaining at time t, [$\text{mg}\cdot\text{kg}^{-1}$]; error bars are for standard errors computed from
75 6 data points).

76 **Figure 3:** Amount of DTPA-extractable Cu over *short-term* (35 days) from the *non-chelated*
77 *system* fitted to (a) zero order, (b) first order, (c) second order, and (d) power function models
78 ($q_t =$ amount remaining at time t, [$\text{mg}\cdot\text{kg}^{-1}$]; error bars are for standard errors computed from
79 6 data points).

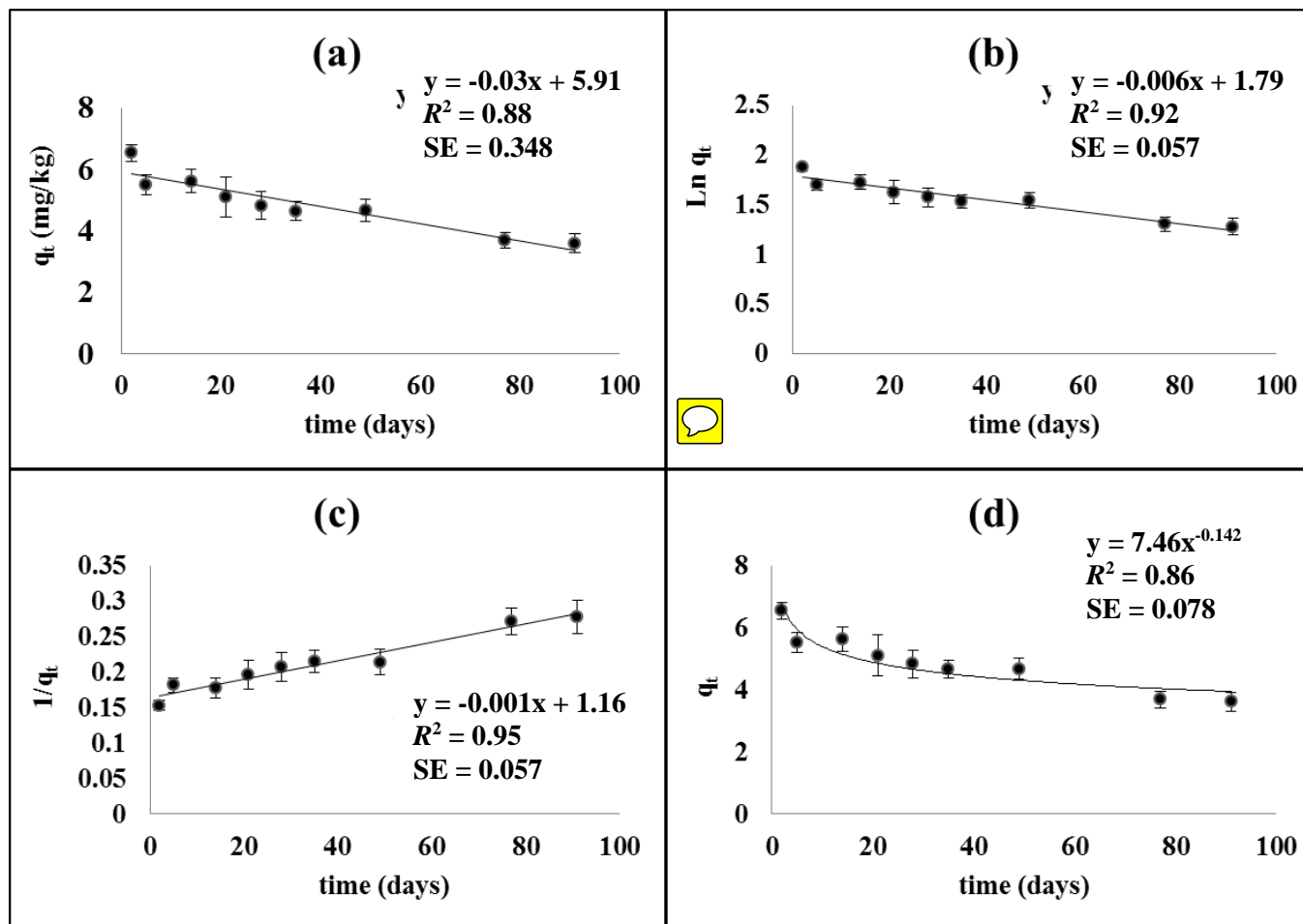
80 **Figure 4:** Amount of DTPA-extractable Cu over *short-term* (35 days) from the *chelated*
81 *system* fitted to (a) zero order, (b) first order, (c) second order, and (d) power function
82 models($q_t =$ amount remaining at time t, [$\text{mg}\cdot\text{kg}^{-1}$]; error bars are for standard errors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

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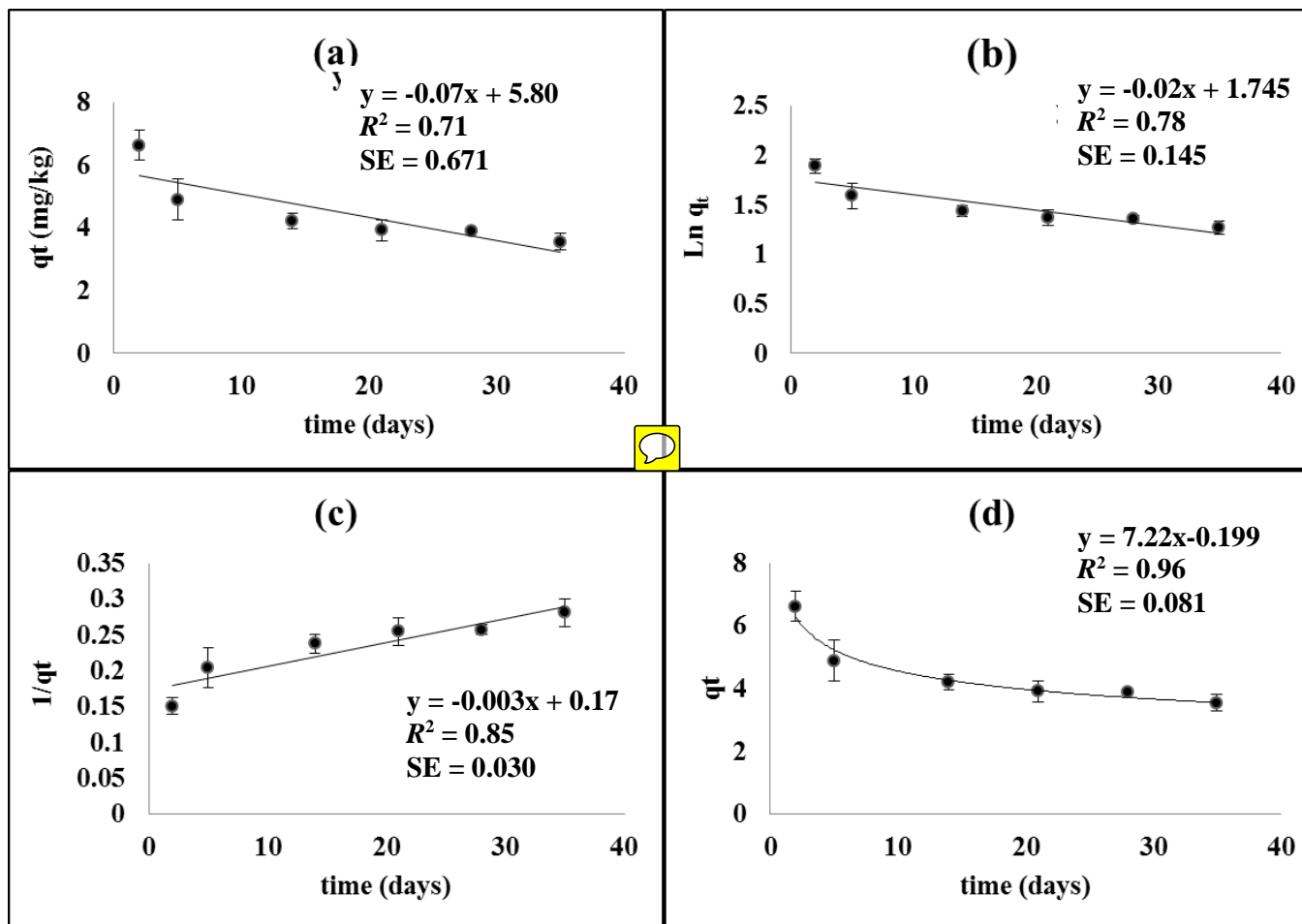
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89 **Figure 1:** Amount of DTPA-extractable Cu over *long-term* (90 days) from the *non-chelated* system fitted to (a) zero order, (b) first
 90 order, (c) second order, and (d) power function (q_t = amount remaining at time t , [$\text{mg}\cdot\text{kg}^{-1}$];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



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

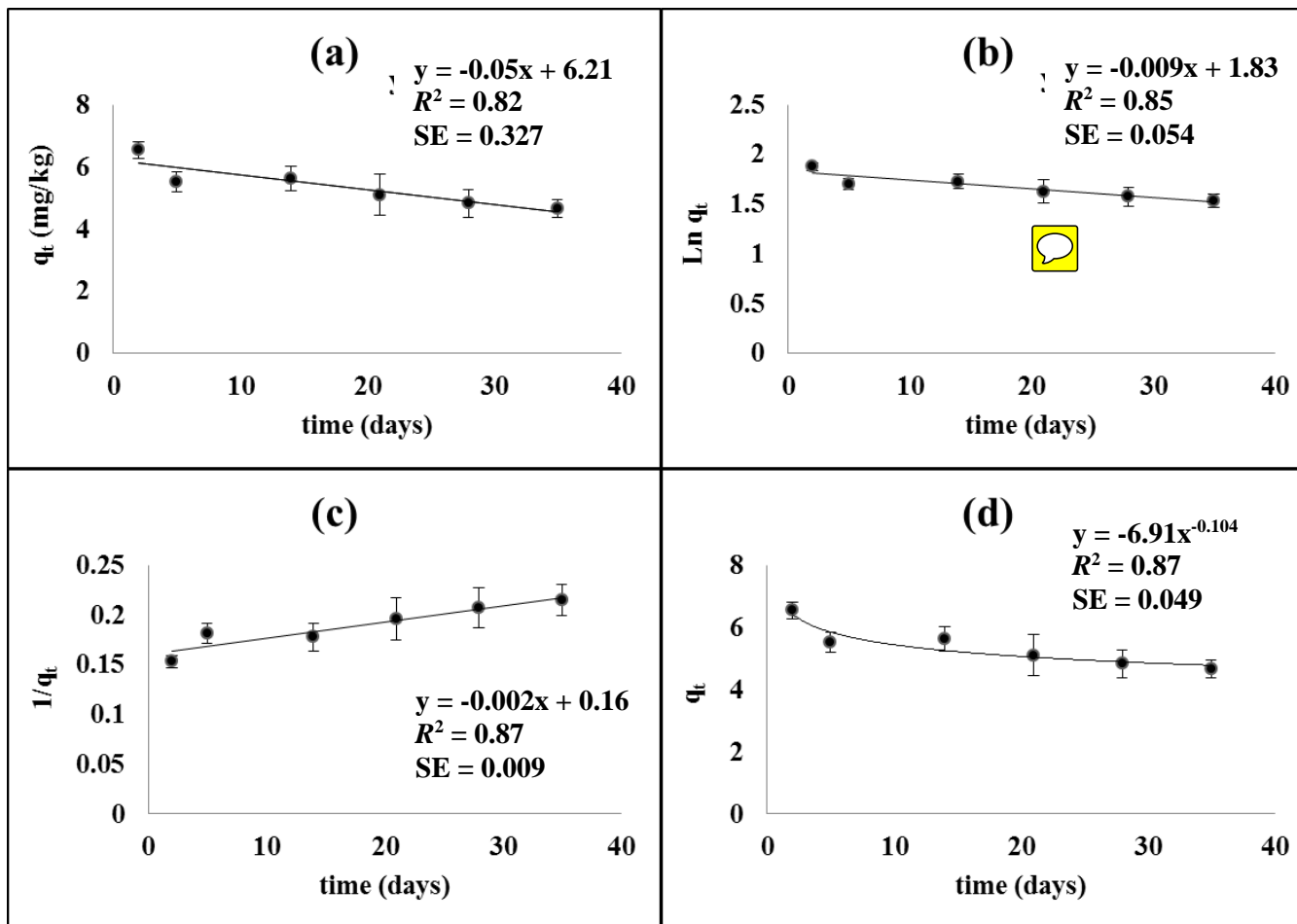


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97 **Figure 3:** Amount of DTPA-extractable Cu over *short-term* (35 days) from the *non-chelated system* fitted to (a) zero order, (b) first
 98 order, (c) second order, and (d) power function models (q_t = amount remaining at time t , [$\text{mg}\cdot\text{kg}^{-1}$];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

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