1 **Fixation kinetics of chelated and non-chelated zinc in semi-arid alkaline soils:**

2 **Application to zinc management**

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27   **Abstract**

28   This study was designed to examine the fixation patterns and kinetics of zinc (Zn) in

29   chelated (Ethylene diamine tetraacetic acid, EDTA) and non-chelated mixed micronutrient

30   systems in semi-arid alkaline soils of the Southern High Plains, US. Soils were characterized

31   for a suite of chemical and physical properties and data obtained from extraction experiments

32   fitted to various kinetic models. About 30% more plant-available Zn was fixed in the non-

33   chelated system within the first 14 d with only about 18% difference observed between the

34   two systems by day 90, suggesting that the effectiveness of the chelated compounds tended to

35   decrease over time. The strengths of the relationships of change in available Zn with respect

36   to other micronutrients (copper, iron, and manganese) were higher and more significant in the

37   non-chelated system (R^2: 0.68-0.94), compared to the chelated (R^2: 0.20-0.77). Fixation of

38   plant-available Zn was best described by the power function model ($R^2 = 0.94$, SE = 0.076) in

39   the non-chelated system, and was poorly described by all the models examined in the chelated

40   system. Reaction rate constants and relationships generated from this study can serve as

41   important tools for micronutrient management and for future micronutrient modeling studies

42   in these soils and other semi-arid regions of the world.

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44   **Keywords:** West Texas, ethylene diamine tetraacetic acid, soil fertility, micronutrients, power

45   function models

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1 Introduction

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51   The soil, a subject of interdisciplinary study (Brevik, et al., 2015), has numerous

52 ecological functions, among which is the storage and cycling of plant needed nutrients (Smith

53 et al., 2015). Micronutrient fixation, a process that leads to the reduction of plant-available

54 portion of micronutrients through its interactions with other soils constituents, limits crop

55 productivity in most part of the world (WHO, 2000). Plant available portion of micronutrient

56 is generally controlled by a number of factors such as soil organic matter (OM), clay, calcium

57 carbonate ($CaCO_3$), and iron (Fe) oxides contents, as well as pH, aeration status, and

58 interaction with other micronutrients (Dimkpa, et al., 2013; Bindraban et al., 2015). Reduction

59 in the availability of micronutrient could be more pronounced in calcareous or alkaline soils

60 due to their inherently high pH (Alloway, 2008; Havlin et al., 2013) which often results in

61 decrease in solubility of most metals, leading to increased fixation of most micronutrients

62 such as copper (Cu), Fe, manganese (Mn), and zinc (Zn) in soil systems (Sparks, 2003). For

63 Zn, apart from high pH; free $CaCO_3$, low OM, and texture could also influence the plant-

64 available portion (Fageria et al., 2002; Alloway, 2008; Alloway, 2009). Climatic and/or

65 environmental conditions such as flooding, temperature variation (cool or wet season) could

66 also affect Zn availability to plants (Slaton et al., 2005; Alloway, 2008; Alloway, 2009;

67 Havlin et al., 2013).

68   Given the ease of fixation in soil, micronutrients such as Zn are often recommended to

69 be applied in the forms of organic or synthetic chelates to enhance their availability to plants.

70 The chemistry and effectiveness of chelated micronutrient compounds have also been

71 previously documented under certain soil conditions and types (Sekhon, 2003; Luo et al.,

72   2005; Chiu et al., 2005; Lucena et al., 2008). However, due to the heterogeneous nature of

73   soils, it could be misleading to apply findings from one soil type and region to another, thus

74   the need for soil- and site-specific studies.

75   As with other arid to semi-arid regions of the world, the Southern High Plains (SHP)

76   of the US is currently facing numerous environmental challenges such as drought, soil

77   salinization, and wind erosion that limit agricultural productivity (Mehta et al., 2000; Stout,

78   2001; Allen et al., 2005). This region is typified by semi-arid climatic conditions with soil

79   types which are characteristically alkaline in nature. Thus, the characteristically high pH soils

80   and climatic conditions of this region favor micronutrient deficiency. Recent field

81   observations have also confirmed cases of limited crop productivity resulting from low level

82   of micronutrients, particularly Zn in some important agricultural soils in Texas High Plains.

83   Unfortunately, in spite of the agronomic significance of the soils of this region, there is still

84   little information on the chemistry of micronutrients in the semi-arid alkaline soils of this

85   regions (Udeigwe et al., 2016). Examining the fixation kinetics of micronutrients in these

86   soils are vital for understanding micronutrient dynamics for further development of nutrient

87   management tools for long-term agricultural and environmental sustainability. Kinetic

88   parameters obtained from such efforts can be used for comparisons among micronutrients as

89   well as among soil types. A more systematic approach to study micronutrients in soil systems

90   will encompass examining their chemistry in a mixed system of a number of other

91   micronutrients. Simple relationships developed from such examination could be used for

92   future predictive purposes.

93   A major limitation to previous studies (Manouchehri et al., 2006; Reyhanitabar and

94   Gilkes, 2010; Abbas and Salem, 2011) on micronutrient fixation was that the experimental

95   conditions (e.g. sample size, reaction times, experimental duration) limits the application of

96   findings to field settings. Extensive literature search on these semi-arid soils indicates that

97   limited resources are available to address: (i) how much of applied plant-available Zn will be

98   present at a specific time, (ii) the reaction rates and mechanism of Zn fixation, and (iii) how

99   these compare to those of other micronutrients, and (iv) how they vary among chelated and

100   non-chelated micronutrient compounds. The objective of this study was to examine the

101   fixation pattern and kinetics of plant-available Zn in chelated (Ethylene diamine tetraacetic

102   acid, EDTA) and non-chelated mixed systems of selected agriculturally-important soils of the

103   SHP, US. The experimental conditions of this study will facilitate the easier application of

104   findings to field settings. Findings are intended to enhance the understanding of Zn chemistry

105   and management in the semi-arid regions.

106   **2   Materials and Methods**

107   **2.1 Site and soil sampling description**

108   Soil samples of interest were collected from three different crop production sites in

109   West Texas. These soils were identified using the Web Soil Survey (WSS) of the Natural

110   Resources Conservation Services (NRCS). Surface (0-15 cm) and subsurface (15-30 cm) soils

111   were collected from three important soil series in the SHP. The soil series include the

112   Amarillo (A), Pullman (P), and Mansker (M) and their descriptions are presented in Table 1.

113   The selected depths are the typical ones examined in most soil fertility and nutrient

114   management studies (Havlin et al., 2013). Soil samples were randomly collected from

115   approximately 12-15 spots at each representative site, using a digging spade marked at 0-15

116   cm and 15-30 cm depths. Samples from the same depth at each site were combined to get a

117   composite sample of about 10 kg. Samplings were sometimes restricted to a defined area of

118   approximately 5-7 ha to avoid crossing into a different soil series.

119   **2.2 Soil property characterization**

120   From each original (untreated) soil sample, a subsample of approximately 2 kg was

121   ground, passed through a 2-mm sieve and stored in plastic bags at a room temperature of

122   approximately 23°C. The samples were then analyzed for a suite of chemical and physical

123   properties. Soil $pH_{1:2}$ and $EC_{1:2}$ were determined on a 1:2 soil/water ratio following the

124   procedure described by Sparks et al. (1996). Soil OM content was determined using the loss

125   on ignition (LOI) method (Nelson and Sommers, 1996). Calcium carbonate content was

126   determined using the tensimeter method 4E and 4E1 of the United State Department of

127   Agriculture NRCS-Soil Survey Investigation Report (Soil Survey Staff, 2014). Particle size

128   determination was conducted using the modified hydrometer method (Gee and Bauder, 1986).

129   Estimation of plant-available micronutrients (Cu, Fe, Mn, and Zn) was conducted using DTPA

130   extraction following the procedure by Lindsay and Norvell (1978). Soil-test P determination

131   was conducted using the Mehlich 3 procedure (Mehlich, 1984). Total elemental content was

132   determined following USEPA Method 3050B using the DigiPREP Digestion System.

133   Measurement of elements in all extracts was conducted using the inductively coupled plasma-

134   optical emission spectroscopy (ICP-OES) (iCAP 7400, Thermo Scientific, Waltham, MA).

135   **2.3 Soil sample preparation and treatment application**

136   Soil sample from each depth was thoroughly mixed and a representative portion taken

137   to fill a 4-L plastic pot. Each pot was planted with sorghum (*Sorghum bicolor*) and grown in

138   the greenhouse with no nutrients added for about 35 d, an optional practice primarily aimed

139   at further depleting the original micronutrient nutrient level of the soils prior to the

140   micronutrient treatment application. After this practice, samples were crushed, air dried,

141   ground, mixed, and passed through a 2-mm sieve. From each soil sample, two subsets of 250

142   g samples were weighed. One set was treated with a mixture of non-chelated micronutrients

143   and the other with a mixture of chelated micronutrients. This was accomplished by using 80

144   ml solution of each fertilizer compound mixture prepared to deliver 5 mg of each

145   micronutrient (Cu, Mn, Zn, and Fe) to 1 kg of each soil. The non-chelated micronutrient

146   compounds used were $CuSO_4 \cdot 5\ H_2O$, $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot H_2O$, and $FeSO_4 \cdot 7\ H_2O$, while

147   the chelated compounds were Cu-EDTA, Mn-EDTA, Zn-EDTA, and Fe-EDTA. Twelve

148   soil-fertilizer treatments were obtained from six soil samples (three soil series by two depths)

149   and two sets of micronutrient amendments (non-chelated mixture and chelated mixture) and

150   each replicated twice for a total of 24 experimental samples. These experimental samples

151   were left in an open space in the laboratory under room temperature of approximately 23°C.

152   Subsamples were taken from each experimental sample at 2, 5, 7, 14, 21, 28, 35, 49, 63, 77,

153   and 90 d and analyzed for plant available-micronutrients using DTPA extraction technique

154   (Lindsay and Norvell, 1978). Following each subsampling event, the remaining soil samples

155   were wetted with water to approximately field capacity. The soils were wetted after each

156   subsampling event within the first 7 d, however, after the first 7 d, sampling was conducted

157   at 7-14 d intervals, thus, the soil samples were wetted every 7 d. The periodic wetting and

158   drying was to simulate field conditions and also provide a medium that will facilitate soil

159   chemical reactions.

2.4 Extraction procedure

161   Preparation of the DTPA extractant and the extraction procedure used followed the

method described by Lindsay and Norvell (1978). The DTPA extraction technique is the most

commonly and broadly used approach for estimating plant-available micronutrient cations

such as Fe, Mn, Cu, and Zn (Liang and Karamanos, 1993). In brief, 20 ml of DTPA extracting

solution was added to 10 g of air-dried soil sample in a 50-mL plastic tube. All tubes were

shaken on a reciprocal shaker for 2 h at approximately 25°C and 180 oscillations per min.

Following shaking, the suspensions were centrifuged for 10 min at 4000 rpm and the resulting

solutions filtered using Whatman 2 filter papers into 16-mm borosilicate glass tubes. All

extractions were 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). The calibration of the ICP-OES instrument was performed using calibration

standards and routinely checked using a set of second source standards from a different

manufacturer. As part of the quality control/quality assurance measures, check samples were

inserted after every 20-25 samples and also the relative percentage difference (RPD) between

duplicates were examined and 10% set as the acceptance criterion.

2.5 Statistical analyses

178   Statistical analyses were performed using the Statistical Analysis Software (SAS 9.4,

SAS Institute, Cary, NC). Differences among means, where applicable, were examined using

180   PROC GLM and mean comparison conducted using Fisher's Least Significance Difference at

181   α level of 0.05. The PROC REG procedure was used to conduct single linear regression

182   analyses used in examining changes in available Zn with respect to other micronutrients in

183   each system (chelated and non-chelated). The data obtained from the kinetic experiment were

184   fitted to selected kinetic models (Table 4) to derive the needed parameters using the PROC

185   NLIN procedure.

186   **3   Results and discussion**

187   **3.1 Soil properties**

188

189   The description and selected properties of the soils used in the study are summarized

190   in Table 1. The average soil pH was 8.05 and pH tended to be higher in the subsurface depth

191   (15-30 cm) of each of the soil series (Mansker, Amarillo, and Pullman). Soil OM ranged from

192   0.93 to 1.57% among depth with an average of 1.33%. This average value is typical of the

193   soils of the area (Udeigwe et al., 2015). The soil EC was within a narrow range of 0.22-0.27

194   dS m^{-1} with an average of 0.24 dS m^{-1}, indicating the studied soils are not salt impacted.

195   Percent $CaCO_3$ varies from 0.13 to 5.59% among depths and was almost two folds higher in

196   the subsurface depths in the Amarillo and Pullman soils. The average clay content within the

197   0-15 cm and 15-30 cm depths were 26.2 and 32.9%, respectively, and the textural classes vary

198   from sandy loam (Amarillo) to clay (Mansker) (Table 1).

199   The results of the total elemental analysis are summarized in Table 2. The observed

200   total content of Fe, Cu, Mn, and Zn were within the typical levels found in most non-polluted

201   agricultural soils or those not receiving excessive amount of organic/inorganic amendments

202   (Adriano, 2001; Kabata-Pendias, 2010), likewise, the levels of Ca, Mg, Na, K, and P

203 (Adriano, 2001; Udeigwe et al., 2009). There appeared to be no consistent trend in the

204 concentration of the elements with depth in each soil series and none of the soils was

205 consistently higher in all the elements measured. Estimated background levels of available

206 nutrients are presented in Table 3. The mean DTPA-extractable Fe, Mn, Cu, and Zn are 5.18,

207 5.09, 0.76, and 0.35 mg kg^{-1}, respectively, likely suggesting an insufficient level of these

208 nutrients (Havlin et al., 2013) in the studied semi-arid soils. Soil-test P varied more widely,

209 ranging from 8.93 to 123 mg kg^{-1}, and was generally higher in the top soil. Phosphorus, a

210 macronutrient could possibly be added through fertilization to these soils.

211 **3.2 Short and long-term zinc fixation pattern**

212   Percent estimates of fixed plant-available Zn determined after the first 14 d

213 (designated as short term), and 90 d (long term) are presented in Table 4. Individual soils and

214 depths were examined, however, findings reveal no justifiable differences among the soils

215 worth discussing, thus, the findings are summarized as averages of all soils within a given

216 depth and for both depths. The percent amount fixed was approximated using the differences

217 between days 2 and 14, and days 2 and 90 for the 14 d and 90 d examinations Comparison

218 was made between the chelated and non-chelated micronutrient treatments. Average values

219 from the three soil series examined revealed that within the non-chelated system,

220 approximately 31.3 and 41.3% of the added Zn was fixed in the 0-15 cm and 15-30 cm

221 depths, respectively, after the first 14 d. When compared to the chelated system, these

222 numbers were drastically reduced to 5.1 % and 6.8 % in the 0-15 and 15-30 cm depths,

223 respectively. After the first 14 d, the averages for both depths were 36.3 % and 6.0 % for non-

224 chelated and chelated systems, respectively. The findings clearly indicate that chelating with

225   EDTA reduced the amount of plant-available Zn fixed by soil constituents (Lopez-Valdivia et

226   al., 2002; Chiu et al., 2005; Alvarez and Gonzalez, 2006). This observed difference between

227   the chelated and non-chelated partly supports the high fixation of Zn encountered in most

228   alkaline soil, particularly when applied non-chelated and why Zn is often the most deficient

229   micronutrient in most alkaline soils (Alloway, 2008).

230   The amount of Zn fixed by the end of the experimental period of 90 d (long-term

231   fixation) was also examined. About 51.1% and 61.4% of available Zn was fixed after 90 d in

232   the non-chelated system within the 0-15 and 15-30 cm depths, respectively. These numbers

233   when compared to the chelated system were 30.7% and 45.1% for the 0-15 and 15-30 cm

234   depths, respectively. Average fixation for both depths in these semi-arid soils after 90 d were

235   56.2% for non-chelated system and 37.9% for chelated system, a difference of approximately

236   18% compared to the 30% observed in the short term fixation (14 d). The narrower

237   differences in Zn fixation observed on the long term could be attributed to the half-life of the

238   chelating agent, EDTA. A half-life of 39 to 59 d for EDTA in doses of 0.8 to 1.6 mmol in a

239   heavy metal phytoextraction study was estimated by Meers et al. (2005), suggesting that the

240   effectiveness of EDTA on micronutrient mobilization will decrease over time, causing more

241   micronutrient to be fixed by other soil constituents. Although not significant, the slightly

242   higher fixation of Zn observed in the subsurface soil could be partly attributed to higher clay

243   content. Clay interaction with metal cations such as Zn, which could reduce the amount of

244   plant-extractable Zn, has been widely documented (Sparks, 2003; Eze et al., 2010; Udeigwe et

245   al., 2015).

3.3 Changes in available zinc with respect to other micronutrients

The changes in the concentration of plant-available Zn over the experimental period of 90 d was compared to those of other micronutrients in both the chelated and non-chelated systems (Table 5). The relationships were examined among individual soil and depth, however, there was no remarkable differences among soils worth discussing, thus, the findings are summarized as averages for the soils at each depth and for both depths combined within each Zn system (chelated and non-chelated). The strengths of the relationships and slope of change between Zn and each of the other micronutrient elements (Cu, Fe, and Mn) were examined using regression analyses. Within each depth, the amount of available Zn positively and significantly changes with each of the other micronutrients, although to a varying degree within the chelated and non-chelated micronutrient systems. 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: 0.20-0.77), suggesting less linearity in changes in Zn concentration to those of the other micronutrients in the chelated system. The slopes were also generally higher in the non-chelated systems for each of the relationships examined, suggesting that more Zn will be fixed for each unit of the other micronutrient fixed in the non-chelated system. Within each depth in the non-chelated system, the change in available Zn with respect to change in Cu (Zn-Cu) was higher than those of Zn-Fe, and Zn-Mn as evidenced from the slopes of the equation. When both depths were combined for each element, within the non-chelated system, the slopes were 0.90 (Zn-Cu), 0.37 (Zn-Fe), and 0.29 (Cu-Zn). Similar relationships were also evidenced in the non-chelated system, although to a lesser strength and some were not significant (Table 5). Within the non-chelated system,

268   the findings suggest that a 1 mg kg^{-1} change in the concentration of available Cu, Fe, and Mn,

269   will be associated with 0.90, 0.37, and 0.29 mg kg^{-1} change in available Zn respectively, in

270   these semi-arid alkaline soils of the SHP. The strong association of Zn and Cu fixation

271   evidenced here could be attributed to the fact these are the two most-limiting micronutrients

272   in these soils with estimated plant-available averages 0.38 and 0.81 mg kg^{-1}, respectively.

273   These relationships provide an estimation of how Zn changes with the other micronutrients in

274   both the chelated and non-chelated systems in this semi-arid alkaline soils. Such information

275   is currently not available for soils of this region and as such little comparisons could be made

276   between the findings here and existing literature.

277   **3.4 Kinetics of zinc fixation**

278   Fixation kinetics of chelated and non-chelated Zn fixation in these soils were further

279   examined by fitting the data obtained from kinetic experiments to various kinetic models. A

280   number of kinetic models (Table 6) were examined, based on the experimental conditions of

281   this study and evidence gathered from previous related studies (Dang et al., 1994;

282   Reyhanitabar and Gilkes, 2010). The criteria used for evaluating best fit among the models

283   were coefficient of determination (R^2) and standard error (SE) (Dang et al., 1994;

284   Reyhanitabar and Gilkes, 2010). Fixation kinetics were studied within soils and depths,

285   however, the individual examination of soils however did not show justifiable reasons to

286   focus the discussion on the comparison among them, thus, for further examinations, average

287   data points for all three soils were used.

288   The data from Zn kinetic experiments were fitted to the zero, first, second order, and

289   power function models and findings summarized in Table 7 . In all the models, **qt** represents

290   the amount of DTPA extractable (plant-available) micronutrient in mg kg^{-1} remaining at time

291   **t**, in d. Discussions will be concentrated on models derived using data points from both depths

292   averaged across soils because there was no difference of interest between the 0-15 and 15-30

293   cm depths that worth focusing the discussion on. Employing more data points will also

294   enhance the statistical reliability of the evaluation. In the non-chelated system, fixation of

295   available Zn was poorly described by the zero, first, and second order models (R^2: 0.66 - 0.82)

296   but better described by the power function model ($R^2 = 0.95$, SE = 0.076) (Fig. 1). This better

297   fit to the power function model suggest that the fixation of plant-available Zn in this mixed

298   system of non-chelated micronutrients is not linear over the experimental period of 90 days

299   (Fig. 1), an indication of a more complex reaction type This finding can be related those of

300   Reyhanitabar et al. (2010) who reported the kinetics of DTPA extraction of zinc from

301   calcareous soils was better described by the power function model. Same was the case when

302   Zn was examined in a single system (data not shown). Within the chelated system (Fig. 2),

303   none of the models examined was able to reasonably describe the reduction of plant-available

304   Zn in these semi-arid soils (R^2: 0.66 to 0.70), a finding suggesting that the reduction of

305   chelated Zn did not perfectly follow the speculated decay trend in these soils over the 90-day

306   period. Literature search did not yield much information on the fixation kinetics of chelated

307   Zn, thus, further justifying the need for this study.

308   **3.5 Significance of findings to zinc management**

309   The fixation kinetics of non-chelated Zn following the power function model over the

310   zero, first, and second order models, is an indication of a more complex reaction type.

311   Inferences drawn from the short and long-term experiments substantiate the need to apply Zn

312   micronutrient in the chelated form on these semi-arid soils as significantly less chelated Zn

313   was fixed particularly within the first 14 d. Findings also highlighted the importance of timing

314   in Zn micronutrient management in these soils even when chelated micronutrient compounds

315   are used. The simple linear relationships of change in plant-available Zn relative to other

316   micronutrients (Cu, Mn, and Fe) could be used as predictive tools. The kinetic parameters

317   obtained from the kinetic experiments could be used for approximating how much of added

318   Zn micronutrient will be available at a given time, particularly for the non-chelated Zn

319   materials which its fixation was reasonably described by the power function model.

320   Findings from this study provide a basis for developing applications for comparing

321   fixation pattern of Zn to those of other micronutrients in a given soil and also among soils. Of

322   interest, the applications developed from this study provide a basis for a more mechanistic

323   approach to evaluating and comparing the fixation patterns and effectiveness of different

324   micronutrient compounds in any given soil system. A database of the reaction rate constants

325   derived for different Zn micronutrient compounds could be used as a tool for making a more

326   informed decision on Zn management on these semi-arid soils, an application that can be

327   extended to soils of other regions.

328   **4 Conclusions**

329   The application of kinetic models to Zn fixation could be used to further the

330   understanding of its chemistry and behavior in the soils of the semi-arid to arid climates. The

331   reduction of plant-available Zn more closely followed the power function models over the

332   zero, first, and second order models in these soils, suggestion a more complex reaction type.

333   Timing is an important practice in Zn management in these semi-arid soils, even when

334   chelated compounds are used. Evidence gathered from this study suggest that kinetic model

335   application to Zn fixation provide a sound basis for evaluating Zn dynamics among soil types

336   and for comparing different Zn micronutrient compounds. The experimental setup and

337   conditions of this study will facilitate the easier application of findings to field settings. This

338   study provides useful background information that will enable future studies on the

339   examination of the reaction mechanisms involved in zinc fixation in chelated and non-

340   chelated systems of these semi-arid soils.

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Table 1. Soil classification and identification of selected semi-arid alkaline soils of the Southern High Plains, USA (Udeigwe et al., 2016)[a]

Soil Series	**Amarillo** (Fine-loamy, mixed, superactive, thermic Aridic Paleustalfs)		**Mansker** (Coarse-loamy, carbonatic, thermic Calcidic Paleustolls)		**Pullman** (Fine, mixed, superactive, thermic Torrertic Paleustolls)	
Sample ID	A_a	A_b	M_a	M_b	P_a	P_b
Depth (cm)	0-15	15-30	0-15	15-30	0-15	15-30
Sampling location	N 33.6058°	W 101.9073°	N 34.1261°	W 101.5899°	N 34.05901°	W 101.4773°
pH	8.07	8.35	8.12	8.20	7.52	8.02
EC (dS m^{-1})	0.24	0.22	0.27	0.25	0.22	0.24
OM (%)	1.05	0.93	1.63	1.24	1.56	1.57
CaCO$_3$ (%)	2.41	5.59	0.98	0.13	2.34	4.16
Clay (%)	17.8	24.0	27.9	41.9	32.8	33.0
Sand (%)	74.9	64.2	56.5	40.9	39.9	38.7
Silt (%)	7.40	11.8	15.6	17.2	27.3	28.3
Textural Class	SL	SCL	SCL	C	CL	CL

[a]SCL, sandy clay loam; SL, sandy loam; CL, clay loam; C, clay; EC, electrical conductivity; OM = organic matter

Table 2. Total elemental analysis of the studied semi-arid alkaline soils of the Southern High Plains, USA (Udeigwe et al., 2016)[a]

Element (mg kg^{-1})	Amarillo		Mansker		Pullman			
	A$_a$	A$_b$	M$_a$	M$_b$	P$_a$	P$_b$	Mean	SD
Al	17187	13823	13808	16840	11571	12943	14362	2215
B	30.9	31.7	35.1	35.1	33.8	33.7	33.4	1.74
Ca	1823	4307	21008	11584	7252	14433	10068	7073
Cu	5.5	5.6	6.1	7.1	6.1	6	6.07	0.57
Fe	11946	9623	9552	11856	8191	8964	10022	1544
K	2848	2791	3004	3554	2926	3029	3025	274
Mg	2537	2205	2341	3103	2015	2199	2400	386
Mn	170	144	135	202	128	130	152	29.1
Mo	1	0.9	6.8	7	0.7	0.7	2.85	3.14
P	375	197	186	158	196	215	221	77.6
Pb	41.1	34.8	33.7	41.5	32.1	33.4	36.1	4.12
Zn	44.5	41.6	51.5	59.1	42.8	41.6	46.9	7.05

[a]SD, standard deviation; a, 0-15 cm; b, 15-30 cm

Table 3. Selected plant-available nutrients in the studied semi-arid alkaline soils of the Southern High Plains, USA (Udeigwe et al., 2016)[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

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

Zn System	Depth[a]	% Fixed after	
	cm	14 days	90 days
Non-chelated	0-15[c]	31.3 (3.0) a	51.1 (9.2) a
	15-30[c]	41.3 (11.5) a	61.4 (4.4) a
	All[d]	36.3 (4.3) A	56.2 (5.9) A
Chelated	0-15[c]	5.1 (2.1) a	30.7 (10.9) a
	15-30[c]	6.8 (2.5) a	45.1 (14.1) a
	All[d]	6.0 (2.3) B	37.9 (7.2) 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 $\alpha = 0\cdot05$).

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

	Cu		Fe		Mn	
			Non Chelated			
0-15	$y = 1.00x - 0.53$	0.92***	$y = 0.35x - 072$	0.86***	$y = 0.25x + 1.46$	0.68**
15-30	$y = 0.82x - 0.60$	0.94***	$y = 0.38x - 0.75$	0.82***	$y = 0.33x + 0.21$	0.73**
All	$y = 0.90x - 0.54$	0.93***	$y = 0.37x - 0.74$	0.88***	$y = 0.29x + 0.84$	0.75**
			Chelated			
0-15	$y = 0.89x + 0.27$	0.77**	$y = 0.20x + 1.86$	0.46*	$y = 0.13x + 3.39$	0.31
15-30	$y = 0.66x + 0.74$	0.42*	$y = 0.15x + 2.60$	0.24	$Y = 0.18x + 2.70$	0.20
All	$y = 0.73x + 0.73$	0.65*	$y = 0.18x + 2.24$	0.47*	$y = 0.14x + 13.14$	0.30

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

Table 6. Kinetic models used for the study of Zn fixation in studied 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	$\mathrm{Ln}\, q_t = \mathrm{Ln}\, q_0 - k_1 t$	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	$q_t = a t^b$	a, initial reaction magnitude constant $[(\mathrm{mg\cdot kg^{-1}}\,(\mathrm{h^{-1}})^b]$ 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. Coefficient of determination (R^2) and standard error (SE) of kinetic models used in examining Zn fixation kinetics in the semi-arid alkaline soils of the SHP, USA[a]

Zinc System	Depth* cm	Zero R^2	Zero SE	First R^2	First SE	Second R^2	Second SE	Power R^2	Power SE
Non-chelated	0-15[c]	0.67	0.703	0.73	0.171	0.77	0.046	0.92	0.092
	15-30[c]	0.59	0.675	0.74	0.169	0.85	0.045	0.91	0.096
	All[d]	0.66	0.655	0.76	0.158	0.83	0.043	0.95	0.076
Chelated	0-15[c]	0.71	0.566	0.69	0.139	0.65	0.037	0.69	0.139
	15-30[c]	0.35	0.808	0.37	0.216	0.38	0.061	0.32	0.224
	All[d]	0.70	0.489	0.70	0.118	0.66	0.030	0.66	0.120

[a] c, n = 3; d, n = 6

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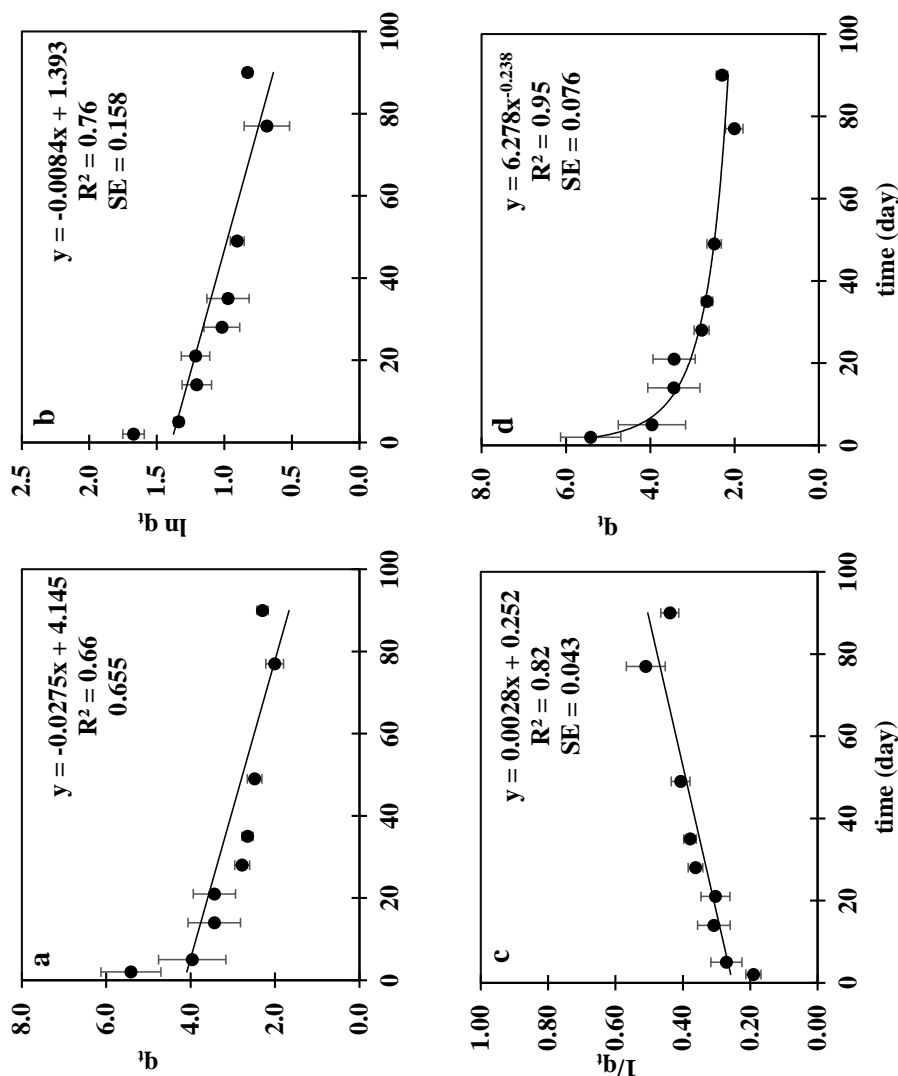
Figure 1. Amount of diethylene triamine pentaacetic acid (DTPA)-extractable Zn over *long-term* (90 days) in the *non-chelated system* fitted to (a) zero order, (b) first order, (c) second order, and (d) power function models (q_t = amount remaining at time t, [mg·kg^{-1}]; error bars are for standard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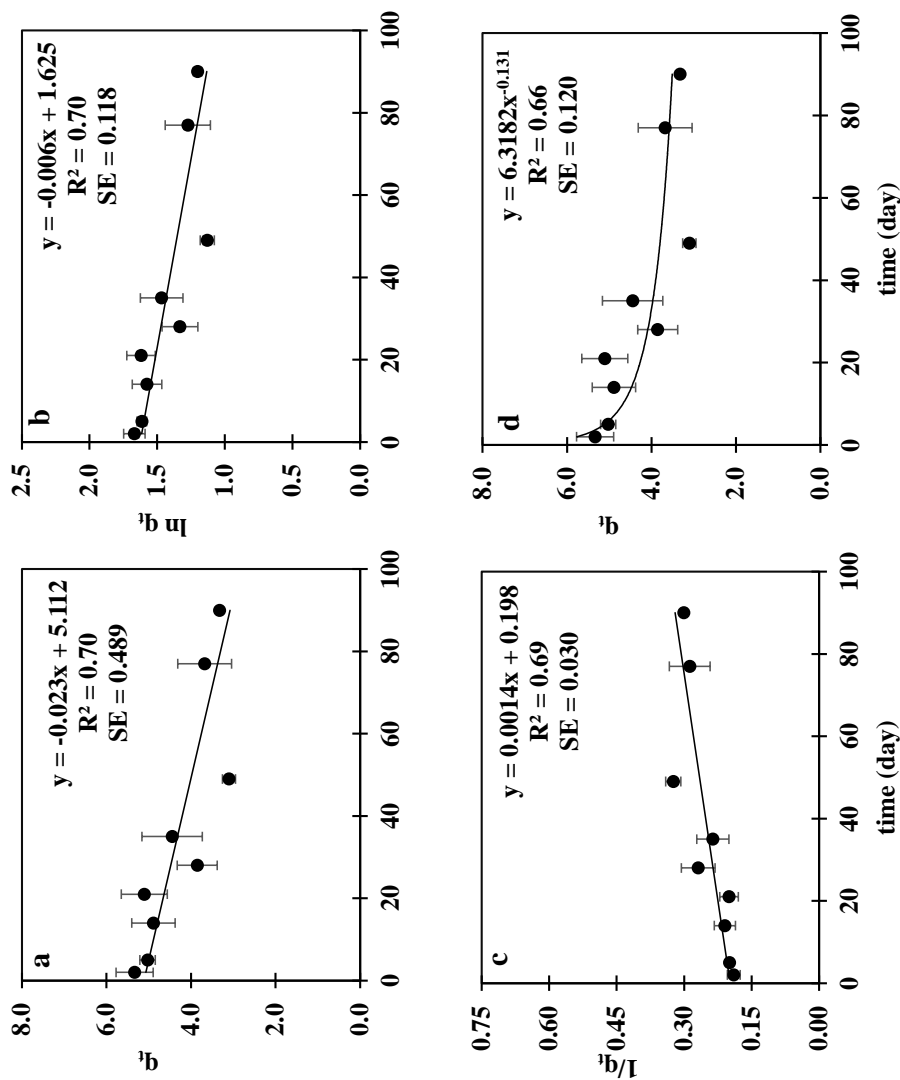
Figure 2. Amount of diethylene triamine pentaacetic acid (DTPA)-extractable Zn over *long-term* (90 days) in the *chelated system* fitted to (a) zero order, (b) first order, (c) second order, and (d) power function models (q_t = amount remaining at time t, [mg·kg^{-1}]; error bars are for standard errors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