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Plant-available zinc fixation kinetics in semi-arid alkaline soils of the Southern High Plains

Theophilus K. Udeigwe^a, Madeleine Eichmann^{a,b}, Peter N. Eze^c, Jasper M. Teboh^d, Gondah M. Zolue^a and Obiageli P. Umeugochukwu^e

^aDepartment of Plant and Soil Science, Texas Tech University, Lubbock, TX, USA; ^bAlbrecht Daniel Thaer-Institut für Agrar- und Gartenbauwissenschaften, Humboldt-Universität zu Berlin, Berlin, Germany; ^cDepartment of Earth and Environmental Science, Botswana International University of Science and Technology, Palapye, Botswana; ^dCarrington Research Extension Center, North Dakota State University, Carrington, ND, USA; ^eDepartment of Soil Science, Stellenbosch University, Matieland, South Africa

ABSTRACT

This study examined zinc (Zn) fixation pattern and kinetics in three semiarid alkaline soils of the Southern High Plains, USA. Soil chemical data obtained from Zn-extraction experiments conducted at different depths were fitted to various kinetic models to examine Zn fixation patterns. Within the experimental period of 90 days, approximately 57% of the total plant-available Zn fixed occurred in the first 14 days when averaged across all soils and depths. Zinc fixation over the experimental period (90 days) was better described by the power function (pfxn) model ($R^2 = 0.87\text{--}0.92$, standard error [SE] = 0.130–0.154), but poorly described by the zero-, first- and second-order models ($R^2 = 0.55\text{--}0.76$, SE = 0.038–0.267). Average reaction rate constant (from the pfxn model) was higher in the subsurface soils (0.323), suggesting a more rapid Zn fixation, compared to the surface soils (0.293). Zinc fixation within the first 35 days was also more rapid and better described by both the second-order ($R^2 = 0.91$, SE = 0.018) and pfxn ($R^2 = 0.92$, SE = 0.119) models. Findings are applicable to field settings and kinetic parameters obtained will help to advance Zn studies and management in these semiarid soils.

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Introduction

The total amount of micronutrients in soil systems is not often a good predictor of the plant-available pool because of nutrient interactions with a number of soil constituents or variables such as pH, organic matter (OM), calcium carbonate (CaCO_3) and clay, which often render them unavailable to plants (Sharma et al. 2004; Ammari & Mengel 2006; Wu et al. 2010; Najafi-Ghiri et al. 2013). Micronutrient chemistry in soil may be influenced by a number of reactions such as complexation with organic and inorganic ligands, ion exchange, adsorption and desorption processes, precipitation and dissolution of solids and acid–base equilibria (Evangelou 1998; Sparks 2003). Thus, micronutrient chemistry could vary depending on soil characteristics and environmental factors.

Zinc (Zn) is a micronutrient that plays a role in enzyme activation, for instance in the synthesis of compound of some proteins and compound for growth hormone production (Havlin et al. 2013). As a heavy metal, it is also of environmental and human health concern (Udeigwe et al. 2015). Like

most other metals, soil solution Zn and the plant-available portion are influenced by soil pH, as solubility tends to decrease with increasing pH. In soil systems, zinc interaction with functional groups such as the carboxyl and phenol of high molecular weight organic compounds in humic and fulvic acids leads to the formation of insoluble complexes; a reaction that reduces the plant-available pool and influences the environmental behavior of Zn (Sparks 2003; Sposito 2008). Other metal (e.g. Cu and Fe) cations could also inhibit the plant uptake of Zn (Havlin et al. 2013). Similarly, high phosphorus (P) level can induce Zn deficiency under certain soil conditions (Fageria 2001; Alloway 2004) as Zn has been shown to bind more strongly to adsorbing surfaces in the presence of P (Kuo & Mikkelsen 1980). Under submerged conditions, Zn concentration does not increase like other micronutrients such as Fe, and this is attributed to increase in pH and the subsequent formation of Zn compounds such as sphalerite (ZnS) (Sajwan & Lindsay 1986; Havlin et al. 2013). Soil temperature also affects Zn availability as its solubility and diffusion increases with temperature (Havlin et al. 2013).

Given the aforementioned interactions of Zn with soil constituents which may lead to the fixation of the plant-available portion, site-specific information is often needed to understand Zn chemistry, environmental fate and availability in a given soil system. Micronutrient fixation, a chemical process that occurs over time, is responsible for the gradual depletion of the plant-available pool. Follett and Lindsay (1971) showed that the reduction of plant-available micronutrients through the process of fixation in soils tends to follow an exponential decay pattern suggesting that the process can be described by kinetic models, such as the zero-, first- and/or second-order models. Information on micronutrient fixation kinetics will help in understanding nutrient dynamics in a given soil system for advanced nutrient management. In addition, kinetic parameters obtained can be used for comparisons among micronutrients, as well as among soils.

The heterogeneity of soils often makes the application of one set of findings from one soil type to another misleading. The Southern High Plains (SHP) of the United States is a region noted for intense agricultural operation. This region produces over 40% of total US cotton (USDA-NASS 2014), and thus of huge agricultural significance. Unfortunately, this region is currently facing complex environmental challenges of drought, wind erosion and soil salinization (Lee et al. 1993; Mehta et al. 2000; Stout 2001; Allen et al. 2005) and recent observations have suggested cases of micronutrient deficiency. Interestingly, there is still insufficient information on the chemistry of micronutrients in the semiarid soils of this region. Previous studies on micronutrients (Kuo & Mikkelsen 1980; Manouchehri et al. 2006; Reyhanitabar & Gilkes 2010; Abbas & Salem 2011) are challenged by some limitations because the experimental conditions, such as sample size, reaction times, sampling times and intervals, limit the application of findings to field settings. This study was initiated because of the limited information on this subject area and the limitations identified in previous studies. Thus, the following questions on Zn chemistry in the semiarid alkaline soils of the SHP remain largely unanswered: (1) How much of applied plant-available Zn will be present at a specific time and (2) what is the reaction rate of Zn fixation, and how does this compare to those of other micronutrients? Thus, the main objective of this study was to examine the fixation pattern and kinetics of plant-available Zn in semiarid alkaline soils. Findings will help to advance the knowledge on Zn chemistry on these semiarid soils and applications developed could help to improve micronutrient management.

Material and methods

Soil description and sampling

Soils of interest to this study were identified using the Web Soil Survey of the Natural Resources Conservation Services. Samples were collected from three different production sites in West Texas

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

Series (classification) ^a	Sample identification	Depth (cm)	Sampling location
Acuff (fine-loamy, mixed, superactive, thermic Aridic Paleustolls)	O _a	0–15	33.8403°N; 101.6999°W
	O _b	15–30	
Amarillo (fine-loamy, mixed, superactive, thermic Aridic Paleustalfs)	A _a	0–15	33.5935°N; 101.9058°W
	A _b	15–30	
Pyron (fine, mixed, superactive, thermic Typic Argiustolls)	Py _a	0–15	32.7211°N; 100.8386°W
	Py _b	15–30	

^aSoil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture: Official Soil Series Descriptions.

at two commonly studied depths of 0–15 and 15–30 cm, covering three agriculturally important soil series [Acuff (O), Amarillo (A) and Pyron (Py)] for a total of six soil samples (Table 1). Soil sample collection was conducted using a digging spade marked to show the selected depths. At each field of 8–12 ha, representative soil samples were collected from 12 to 15 different spots and combined to get a composite sample of about 12 kg of each soil depth. The sampled fields have no history of micronutrient fertilizer treatment.

Sample preparation

About 10 kg of each soil sample was thoroughly mixed and placed in a 4-L plastic pot and sorghum (*Sorghum bicolor*) was grown over a period of 35 days in the greenhouse. This was an optional practice primarily aimed at further depleting the original micronutrient level of the soils prior to treatment application. Following this, the soils were air-dried, thoroughly mixed, ground, passed through a 2-mm sieve and stored in plastic bags at a room temperature of approximately 23°C.

Soil characterization

A portion of each soil sample was analyzed for soil pH, electrical conductivity (EC), OM, CaCO₃, particle size, total elements (Al, Ca, Cu, Fe, K, Mg, Mn, Mo, P, Pb and Zn), soil-test P (Mehlich 3) and diethylene triamine pentaacetic acid (DTPA)-extractable (plant-available) micronutrients (Cu, Zn, Fe and Mn) following approved analytical methods. The DTPA extractant was used in this study for plant-available nutrient estimation because it is commonly used in this region for micronutrient recommendations.

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 method following the procedure by Nelson and Sommers (1996). Percentage of CaCO₃ was determined using the tensimeter method 4E and 4E1 of the US 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). Soil-test P was determined using Mehlich-3 procedure (Mehlich 1984). Estimation of total elements in the soil samples was conducted using the DigiPREP Digestion System (DigiPREP MS, SCP Science, Quebec, Canada) following the US Environmental Protection Agency (USEPA) Method 3050B. Plant-available micronutrients were determined by DTPA extraction following the procedure by Lindsay and Norvell (1978). Measurement of the elements in all extracts was conducted using the inductively coupled plasma-optical emission spectroscopy (ICP-OES) (iCAP 7400, Thermo Scientific, Waltham, MA). All the analyses were conducted in replicates of two.

Soil treatment and plant-available Zn extraction

From each soil sample, 250 g was weighed and treated with 80 mL of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ solution prepared to deliver 10 mg Zn kg^{-1} soil, for a total of six treatments (3 soil series by 2 depths), each replicated twice for a total of 12 samples. All treated samples were kept in an open space in the laboratory and subjected to the same conditions at room temperature. A subsample was taken from each of the 12 treated soil sample at 2, 5, 8, 14, 21, 28, 35, 49, 63, 77 and 90 days and analyzed for plant-available micronutrients using the DTPA-extraction technique. Following each subsampling event, the remaining soils were periodically wetted to approximately 50% of the field capacity to facilitate chemical reactions in the soil and also to simulate the wetting and drying cycle obtainable under field condition. Within the first 7 days, the soils were wetted after each subsampling event. After the first 7 days, sampling was conducted at 7–14 days intervals; thus, the soil samples were watered every 7 days.

The preparation of DTPA extractant and the extraction procedure followed the procedure of Lindsay and Norvell (1978). The DTPA extractant is the most commonly used reagent for estimating plant-available micronutrients such as Cu, Fe, Mn and Zn (Liang & Karamanos 1993). Briefly, 10 g of air-dried soil was placed in a 50-mL plastic tube and 20 mL of DTPA extracting solution added. The tubes were shaken on a reciprocal shaker for 2 h at room temperature and at approximately $180 \text{ oscillations min}^{-1}$. Following shaking, samples were centrifuged for 10 min at 4000 rpm, and the solutions passed through a Whatman No. 2 filter paper and collected in 16-mm boroglass tubes. All filtrates were analyzed for Zn using ICP-OES (iCAP 7400, Thermo Scientific, Waltham, MA) following USEPA Method 200.7 (USEPA-ICP Users Group 1982). The calibration of the ICP-OES was conducted using standard reference materials following the manufacturer's recommendations. Calibration was checked using second source calibration standards from a different vendor. During sample analysis, check samples were also inserted after approximately every 25 samples to monitor instrument stability. Relative percentage difference between duplicates was also calculated and 10% acceptance standard used.

Statistical analyses

Statistical analyses were performed using the Statistical Analysis Software (SAS 9.4, SAS Institute, Cary, NC). Differences among means where applicable were examined using the PROC GLM and mean comparison conducted using Fisher's least significance difference at α level of 0.05. Single and multiple linear regression analyses between available nutrients and soil properties were conducted using the PROC REG procedure. Data obtained from the kinetic studies were fitted to selected kinetic models (Table 6) to derive the needed parameters.

Results and discussion

Soil characteristics

Basic chemical and physical properties of the soils are presented in Table 2. The soils are alkaline with an average pH of 8.30. Soil OM ranged from 0.59% in Amarillo (A_a) to 1.70% in Acuff (O_a) with an average of 1.19%. The average soil $\text{EC}_{1:2}$ value of 0.24 dS m^{-1} suggests that the studied semiarid soils are not saline. The average CaCO_3 content was 2.24%, with the lowest and highest values of 0.46% and 4.68% found in the top soils of Amarillo and Pyron, respectively. The soil textural classes were mostly sandy dominated given the average clay and sand contents of 27% and 60%, respectively (Table 2). Variation in the examined soil properties among these agricultural soils could be ascribed to their geological differences and partly to management practices. The observed properties are typical to those of the soils of the SHP (Udeigwe et al. 2015).

The results of the total elemental analysis are presented in Table 3. The concentration ranges of elements such as Ca, Mg, K and P in these semiarid soils are typical of those of most agricultural

Table 2. Selected soil properties of the studied semiarid alkaline soils of the Southern High Plains, USA.^a

Series	Acuff		Amarillo		Pyron	
	O _a	O _b	A _a	A _b	Py _a	Py _b
pH	8.18	8.24	8.32	8.30	8.39	8.36
EC (dS m ⁻¹)	0.23	0.21	0.17	0.17	0.35	0.27
OM (%)	1.70	1.35	0.59	0.75	1.31	1.43
CaCO ₃ (%)	1.95	1.17	0.46	0.65	4.68	4.55
C (%)	24.7	26.0	19.4	23.2	29.7	37.6
Sand (%)	62.4	61.0	72.4	65.7	49.0	50.7
Silt (%)	12.9	13.0	8.2	11.1	21.3	11.7
Textural class	SCL	SCL	SL	SCL	SCL	SC

^aSCL: Sandy clay loam; SC: sandy clay; SL: sandy loam; CL: clay loam; C: clay; a = 0–15 cm; b = 15–30 cm.

Table 3. Total elemental analysis of the studied semiarid alkaline soils of the Southern High Plains, USA.^a

Series	Soil ID	Al	Ca	Cu	Fe	K	Mg	Mn	Mo	P	Pb	Zn
		mg kg ⁻¹										
Acuff	O _a	18429	8769	6.1	12164	2905	2572	158	1.10	153	43.5	39.8
	O _b	18424	6551	6.2	11997	2680	2641	138	0.90	110	43.5	42.9
Amarillo	A _a	14835	1775	4.9	10596	2578	2270	149	0.90	88.5	37.1	38.9
	A _b	16631	1830	5.3	11601	2824	2468	164	0.90	79.4	40.7	43.6
Pyron	Py _a	21305	19377	7.9	14188	3570	3546	190	1.30	125	50.4	43.2
	Py _b	22359	19031	7.7	14471	3457	3372	183	1.20	110	51.9	43.6
Mean		18664	9556	6.4	12503	3002	2812	164	1.05	111	44.5	42.0
SD		2812	7951	1.2	1519	413	520	19.9	0.18	26.3	5.67	2.09

^aSD: standard deviation; ID: identification.

soils (Chen et al. 1999; Adriano 2001; Udeigwe et al. 2009). Likewise, the concentrations of Fe, Cu, Mn and Zn were within typical background levels found in most soils (Adriano 2001; Kabata-Pendias 2010). The concentration of most of the measured elements (Al, Ca, Cu, Fe, K, Mg, Mn, Mo and Pb) was higher in the Pyron soil compared to the other soils, and this could be attributed to its correspondingly higher average clay content of 34% compared to the average of 25.4% and 21.3% for Acuff and Amarillo soils, respectively.

To understand the interactions among soil constituents in these semiarid soils, a number of relationships were also examined within the limits of this study. Although only six data points were used, the relationships are statistically significant and worth noting for these semiarid soils because they are related to nutrient chemistry. Significant positive correlations were observed between CaCO₃ and each of Al, Cu, Mn, Mo and Pb ($R = 0.86\text{--}0.98$; $P = 0.001\text{--}0.03$, $n = 6$). These correlations suggest that a significant portion of these elements could be bound in the CaCO₃ fractions in these semiarid soils. Metal–carbonate interaction is also widely documented (Sposito et al. 1982; Tack & Verloo 1995; McLaren & Clucas 2001); a process that can affect the availability of metal micronutrient such as Zn. Likewise, soil clay content was positively correlated with each of Al, Ca, Cu, Mg and Pb ($R = 0.86\text{--}0.94$; $P = 0.004\text{--}0.02$, $n = 6$). Soil clay interaction with metals is partly attributed to the abundance of negatively charged sites and high surface area created by clay minerals, leading to high adsorption capacity for most metals (Sparks 2003; Sposito 2008). The strong positive correlations between soil EC and each of Ca, Na and Mg ($R = 0.93\text{--}0.94$, $P = 0.006$, $n = 6$) are indications of the contribution of the salts of these elements to soil EC.

The initial background levels of available nutrients are shown in Table 4. The mean values of DTPA-extractable Fe, Mn, Cu and Zn are 4.08, 4.32, 0.54 and 0.23 mg kg⁻¹, respectively. Soil-test P varied more widely, ranging from 3.89 to 24.3 mg kg⁻¹, and was consistently higher in the 0–15-cm depth, suggesting a possible P input to some of these soils through anthropogenic sources, for example, fertilization and organic residue addition.

Table 4. Estimated plant-available nutrients in the studied semiarid 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				
Acuff	O _a	3.29	4.31	0.54	0.09	7.83
	O _b	4.00	3.55	0.53	0.13	3.89
Amarillo	A _a	3.37	4.67	0.39	0.24	15.7
	A _b	4.46	5.57	0.48	0.17	8.95
Pyron	Py _a	4.13	3.76	0.63	0.40	24.3
	Py _b	5.20	4.07	0.68	0.32	13.2
Mean		4.08	4.32	0.54	0.23	12.3
SD		0.71	0.73	0.10	0.12	7.2

^aDTPA: Diethylene triamine pentaacetic acid; M3: Mehlich 3; SD: standard deviation; ID: identification.

Examination of short- and long-term Zn fixation patterns

Percentage estimates of plant-available Zn fixed in the first 14 days (short term) and over the experimental period of 90 days (long term) were examined for each soil (Table 5). However, the findings were presented as the average for all soils because there were no interesting differences among soils worth discussing. This approach also enhanced the statistical power of the evaluation. Percentage estimates of plant-available Zn were approximated using the differences between the amount of available Zn remaining at days 2 and 14, and days 2 and 90. Within the surface depth (0–15 cm), approximately 31% of the original available Zn was fixed within the first 14 days, with approximately 34% more fixed by the end of the experimental period (day 90). Within the subsurface depth (15–30 cm), close to 45% of the plant-available Zn was fixed in the first 14 days, with the total amount fixed by the end of the experimental period of 90 days approaching 68% (i.e. 23% more). The difference in the amount of Zn fixed between the surface and subsurface soil depths, particularly within the first 14 days, although not statistically different, could be possibly attributed to differences in soil properties such as clay content. This difference tended to narrow out by day 90. When the average fixation in both depths was considered, Zn fixed after 14 days was approximately 37.8% and total amount fixed after 90 days was 66.2% (difference of 28.4%), indicating that close to 57% of the total plant-available Zn fixed within the experimental period was in the first 14 days. The finding here suggests the importance of timing in Zn management in these semiarid alkaline soils as extractability of added Zn tended to decrease with time (Ma & Uren 1997).

Among all the soil properties examined, pH ($R = 0.79$) and total P ($R = 0.45$) showed a slight positive trend with the amount of Zn fixed over the experimental period of 90 days, although these were not significant given the sample size (n) of 6. The relationship between Zn fixation and total P is partly supported by the findings of Kuo and Mikkelsen (1980) who showed that Zn binds more strongly to adsorbing surfaces in the presence of P than in its absence. With respect to pH, the sorption of Zn onto soil constituents, which will in turn reduce the amount of plant-available Zn, will tend to increase with soil pH (Sparks 2003; Havlin et al. 2013).

Table 5. Average percentage (with standard deviation) of plant-available Zn fixed after 14 and 90 days in the studied semiarid alkaline soils of the Southern High Plains, USA.

Depth (cm)	n	Zn fixed (%) after	
		14 days	90 days
0–15	3	30.9 (18.6) a	64.7 (7.60) a
15–30	3	44.8 (20.9) a	67.6 (2.93) a
All	6	37.8 (19.8)	66.2 (5.27)

Mean values in a column with the same lowercase letter are not statistically different (Fisher's LSD $\alpha = 0.05$).

Kinetics of Zn fixation

The data obtained from Zn kinetic experiments were fitted to various kinetic models to further explain the pattern of Zn fixation in the examined soils. Using the findings from previous studies (Dang et al. 1994; Reyhanitabar & Gilkes 2010) and the experimental conditions of this particular study, a number of kinetic models were examined. Those of relevance to this study are presented in Table 6. Examination was made among soils, soil depths (0–15 and 15–30 cm) and also for all soils and depths combined. The criteria used for evaluating the best fit among models were coefficient of determination (R^2) and SE (Dang et al. 1994; Reyhanitabar & Gilkes 2010). If zero order, it implies that the rate of reaction does not depend on the concentration of the reactant (Zn); while first order will imply that the rate of reaction is dependent on the concentration of only one reactant (e.g. Zn); and second order implying that the reaction rate depends on the concentration of two reactants (e.g. Zn and another soil constituents) (Evangelou 1998; Sparks 2003).

The soils were examined individually and the R^2 of kinetic models used in describing micronutrient fixation in each soil over the experimental period of 90 days and a short term of 35 days are presented in Table 7. The shorter term examination was deemed necessary because a closer examination of the data reveal a possible discontinuity in slope or differences in the pattern of the data before and after day 35, indicating a possible difference in the pattern of Zn fixation before and after the first 35 days. Thus, the data points within the first 35 days were isolated and examined separately. In each of the soils examined, Zn fixation within the entire experimental period of 90 days was better described by the power function (pfxn) model ($R^2 = 0.89\text{--}0.91$). Similar observation was made for Zn fixation within the first 35 days, with the exception of the Pyron soil (Table 7). The individual examination of the Zn fixation kinetics for each soil did not show justifiable reasons to focus our discussion on the comparison of soils as earlier intended. Thus, for further examination of Zn fixation, average data points for all soils were used. This approach also helped to enhance the statistical reliability of the findings since more data points were employed. Figures 1 and 2 show the average data, within the experimental period of 90 days, for all soils at 0–15 and 15–30 cm depths, respectively, fitted to the zero-, first-, second-order and pfxn models, where q_t represents the amount of DTPA-extractable (plant-available) Zn remaining at time t in day. The reduction of plant-available Zn was better described by the pfxn model ($R^2 = 0.87\text{--}0.92$, SE = 0.154–0.251) and poorly described by the zero-, first- and second-order models ($R^2 = 0.55\text{--}0.76$, SE = 0.038–0.267) in each depths. The ability of the pfxn model to describe Zn fixation better than the other models (zero, first and second) has also been noted by Dang et al. (1994) and Reyhanitabar and Gilkes (2010) in their study of DTPA extraction kinetics of Zn in calcareous soils. However, the absolute values of reactions rate constants obtained in this study cannot be directly compared to those obtained by these researchers because of the differences in experimental setup and objectives. The better fit to the pfxn model observed here indicates that the fixation of plant-available Zn is not linear in these semiarid alkaline soils within the 90-day experimental duration. A closer examination of the fixation between the two depths, as described by the pfxn model, revealed a higher reaction rate constant of 0.323 in the 15–30 cm compared to 0.292 in the 0–15 cm. This finding supports the

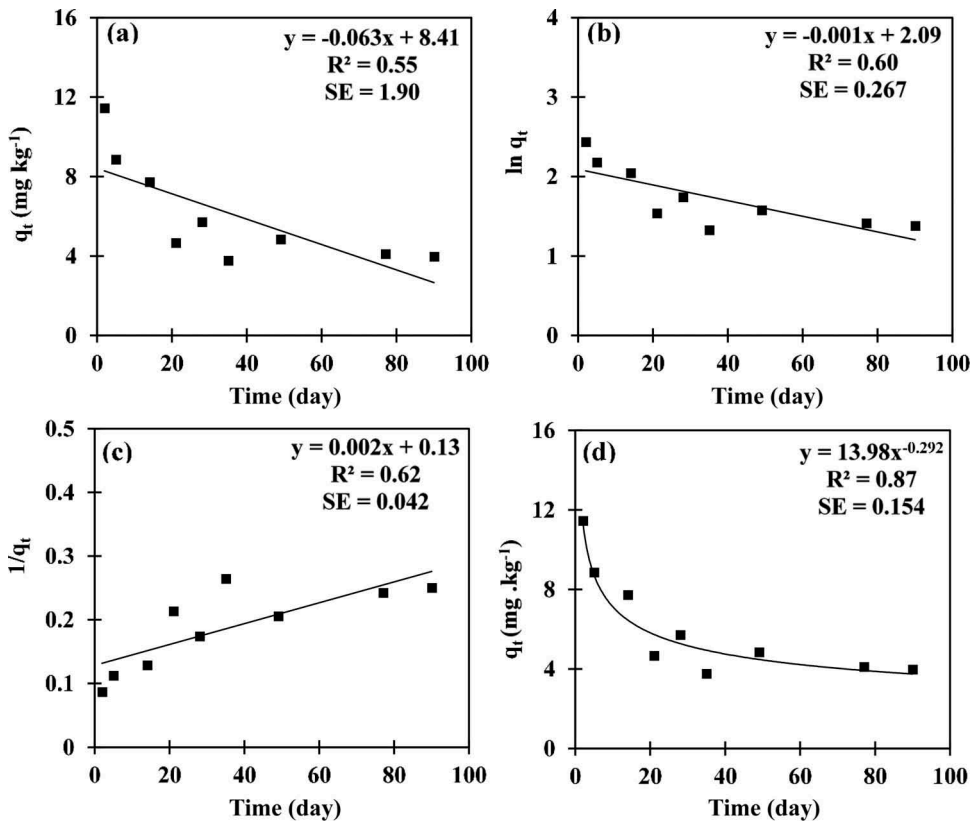
Table 6. Kinetic models used for the study of Zn fixation in the studied semi-arid alkaline soils of the Southern High Plains, USA.^a

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

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

Table 7. Summary of coefficients of determination (R^2) of kinetic models used in describing Zn fixation for experimental periods of 90 and 35 days for the semiarid soils of the Southern High Plains, USA.

	Kinetic models			
	Zero	First	Second	Power
<i>90 days</i>				
Acuff	0.56	0.61	0.65	0.91
Amarillo	0.45	0.6	0.71	0.89
Pyron	0.59	0.67	0.73	0.82
<i>35 days</i>				
Acuff	0.89	0.92	0.91	0.91
Amarillo	0.63	0.77	0.88	0.93
Pyron	0.73	0.76	0.75	0.71

**Figure 1.** Average DTPA-extractable zinc over the experimental period of 90 days within 0–15 cm depth fitted to (a) zero-order, (b) first-order, (c) second-order and (d) power function model (q_t = amount remaining at time t [mg kg^{-1}]).

relatively higher amount of Zn fixed in the 15–30-cm depth compared to the 0–15-cm depth, particularly within the first 14 days (Table 5).

Since there were no striking differences worth focusing on between the two depths, Zn fixation kinetics was further examined using averaged data points from all soils and depths (Figure 3). The findings indicated that likewise, the reaction leading to the fixation of available Zn poorly followed the zero-, first- and second-order model ($R^2 = 0.56$ – 0.75) but was better described by the pfxn model ($R^2 = 0.93$, $SE = 0.109$). On the other hand, findings from Zn

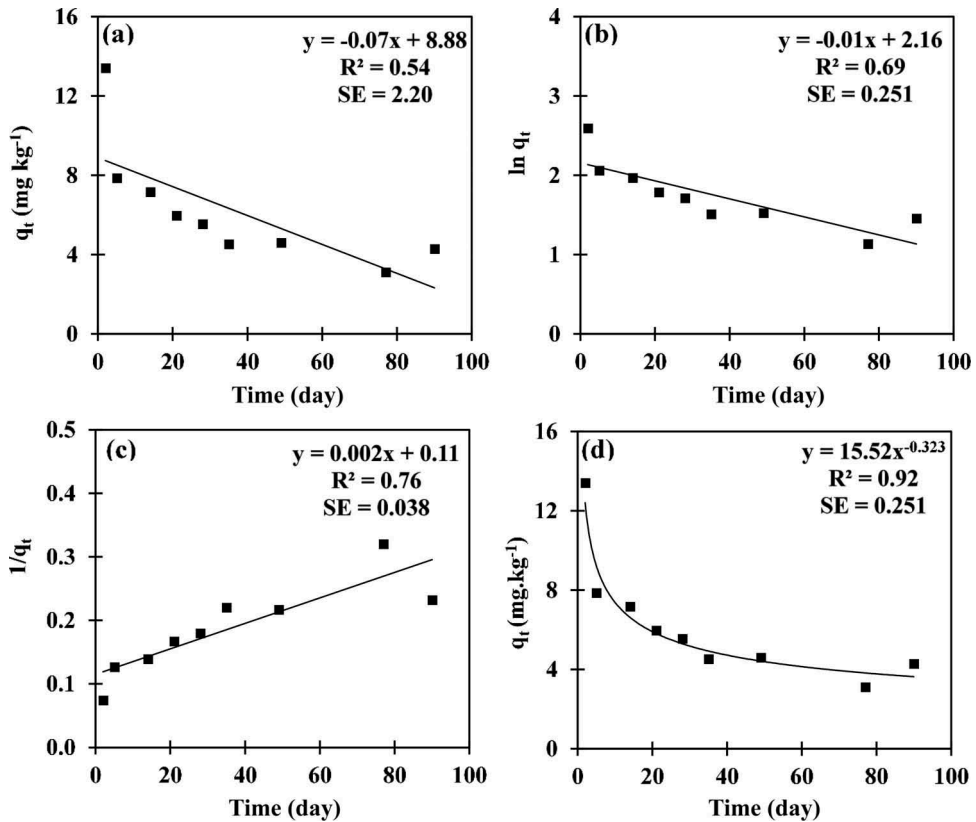


Figure 2. Average DTPA-extractable zinc over the experimental period of 90 days within 15–30 cm depth fitted to (a) zero-order, (b) first-order, (c) second-order and (d) power function model (q_t = amount remaining at time t [mg kg⁻¹]).

fixation within the first 35 days, examined differently, showed that the reduction in the amount of plant-available Zn was better described by both pfxn model ($R^2 = 0.92$, $SE = 0.119$) and second-order model ($R^2 = 0.91$, $SE = 0.018$) (Figure 4). It can be evidenced from the figures that there appear to be a more rapid and somewhat linear decrease in the amount of available Zn within the first 35 days, implying that most of the fixation of available Zn in these semiarid soils will occur approximately within the first 35 days. This finding is supported by the relatively high reaction rate constant of 0.335 observed in the 35-day term compared to the 0.307 for the 90-day experimental period, further stressing the significance of timing in Zn management on these soils.

Application of findings to Zn management

The overall better fit of Zn fixation kinetics to the pfxn model in these semiarid soils is an indication of a more complex fixation pattern. Evidence gathered from the short- and long-term fixation experiments suggests the importance of timing in Zn management on these soils as majority of the available Zn was fixed within the first 35 days. The reaction rate constants were also higher in the first 35 days suggesting faster Zn fixation. The reaction rate constants obtained from this study could be used to approximate how much of added Zn material will be available at a specific point in time. A major application of the findings from this study will be for the comparison of the

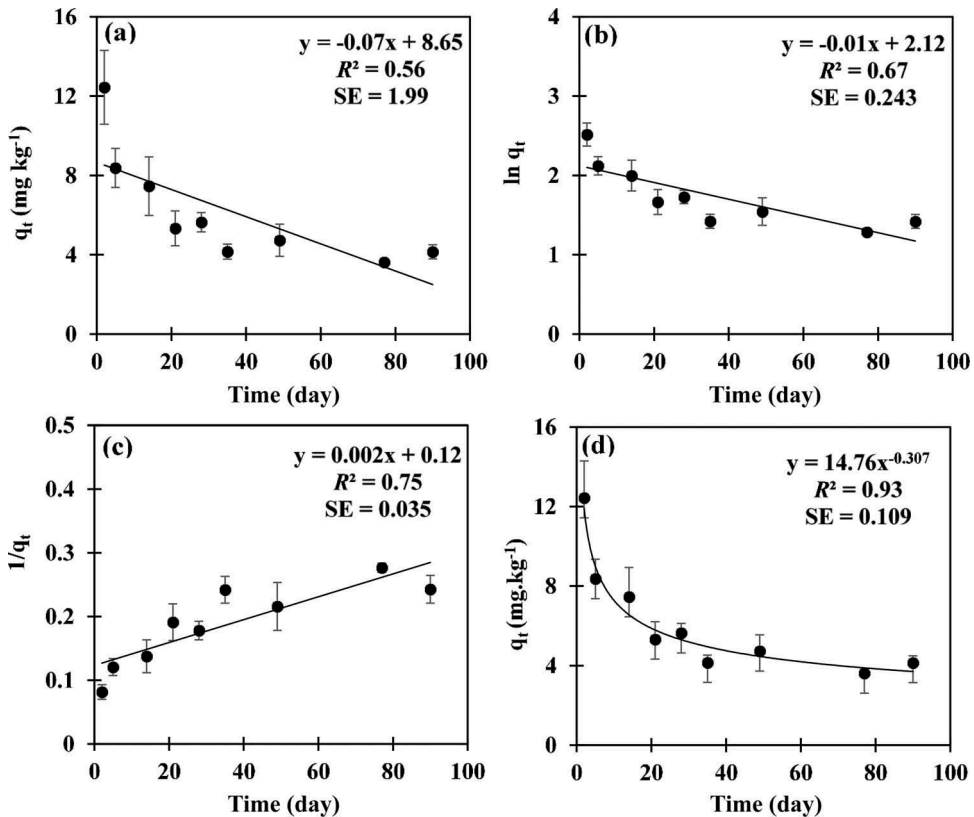


Figure 3. Average DTPA-extractable zinc (average of both depths) over the experimental period of 90 days fitted to (a) zero-order, (b) first-order, (c) second-order and (d) power function model (q_t = amount remaining at time t [mg kg^{-1}]; error bars are for standard deviation computed from six data points).

patterns of Zn fixation to those of other micronutrients within these soils and other soils. Of interest, applications developed from this study lay the foundation for a more mechanistic approach for evaluating and comparing the effectiveness of different Zn micronutrient products, for example, commercial chelated Zn compounds in soils by examining the fixation patterns and kinetic parameters. A database of the reaction rate constants derived for different Zn compounds can be compared among themselves and this information used for making Zn management decisions for these semiarid soils.

Conclusions

A number of soil reactions and thus different mechanisms of interactions are involved in the fixation of plant-available Zn. This study, which examined Zn fixation patterns using common kinetic models applied to the study of soils, suggests that the pfxn model better described the reduction of plant-available Zn in the studied semiarid soils. Kinetic parameters obtained also suggest that Zn fixation rate would be higher within the first 35 days; thus, majority of the Zn will be fixed within that period. A number of future studies that will be enabled by this study include the examination of the reaction mechanisms involved in zinc fixation, as well as examining how these mechanisms and fixation pattern would vary in a chelated Zn system in these semiarid soils. The experimental conditions and design (e.g. the experimental duration of 90 days, wetting and drying cycles and no soil agitation) of this study will facilitate the easier application of findings to field settings.

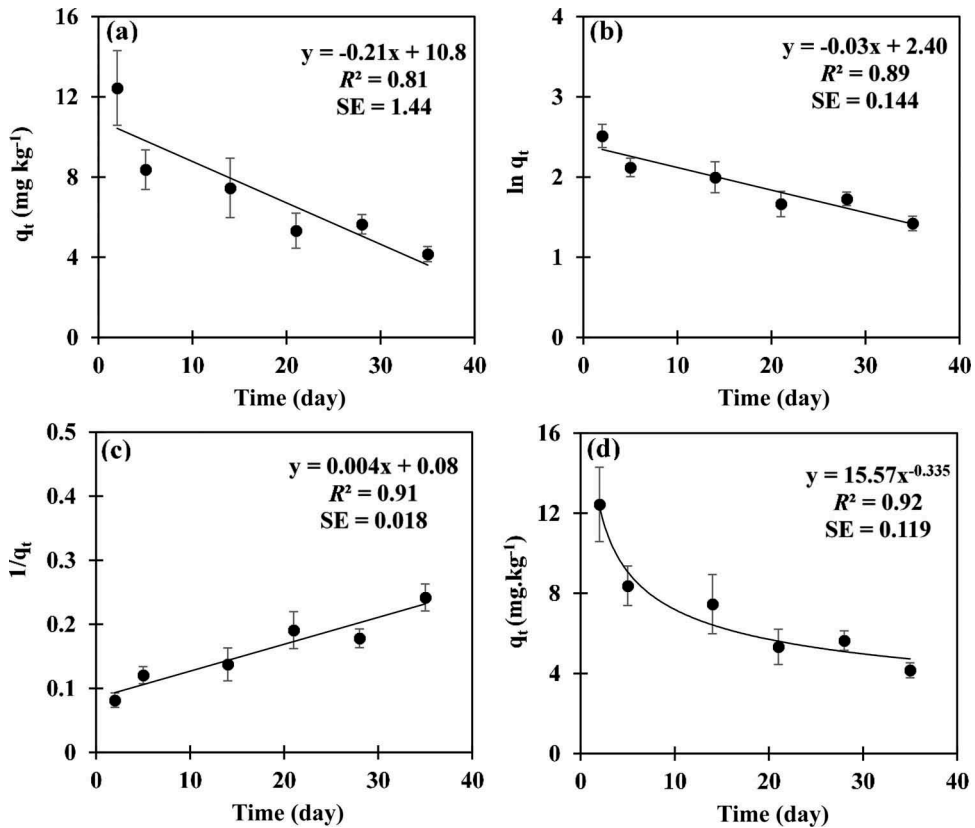


Figure 4. Average DTPA-extractable zinc (average of both depths) within the first 35 days fitted to (a) zero-order, (b) first-order, (c) second-order and (d) power function models (q_t = amount remaining at time t [mg kg^{-1}]; error bars are for standard deviations computed from six data points).

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Disclosure statement

No potential conflict of interest was reported by the authors.

References

- Abbas MH, Salem HM. 2011. Kinetics of iron retention by typic torriorthent and typic haplocalcid soils supplied with some micronutrients. *Ann Agric Sci Moshtohor*. 49:301–311.
- Adriano DC. 2001. Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals. New York (NY): Springer Science and Business Media.
- Allen VG, Brown CP, Kellison R, Segarra E, Wheeler T, Dotray PA, Conkwright JC, Green CJ, Acosta-Martinez V. 2005. Integrating cotton and beef production to reduce water withdrawal from the Ogallala aquifer in the Southern High Plains. *Agron J*. 97:556–567.
- Alloway BJ. 2004. Zinc in soils and crop nutrition. 2nd ed. Brussels: International Zinc Association.
- Ammari T, Mengel K. 2006. Total soluble Fe in soil solutions of chemically different soils. *Geoderma*. 136:876–885.

- Chen M, Ma LQ, Harris WG. 1999. Baseline concentrations of 15 trace elements in Florida surface soils. *J Environ Qual.* 28:1173–1181.
- Dang YP, Dalal RC, Edwards DG, Tiller KG. 1994. Kinetics of zinc desorption from vertisols. *Soil Sci Soc Am J.* 58:1392–1399.
- Evangelou VP. 1998. *Environmental soil and water chemistry: principles and applications.* New York (NY): Wiley.
- Fageria VD. 2001. Nutrient interactions in crop plants. *J Plant Nutr.* 24:1269–1290.
- Follett RH, Lindsay WL. 1971. Changes in DTPA-extractable zinc, iron, manganese, and copper in soils following fertilization. *Soil Sci Soc Am J.* 35:600–602.
- Gee GW, Bauder JW. 1986. Particle-size analysis. In: Klute, A, editor. *Methods of soil analysis. Part 1 – physical and mineralogical methods.* Madison (WI): Soil Science Society of America; p. 383–411.
- Havlin JLT, Nelson SL, Beaton JD. 2013. *Soil fertility and fertilizers. An introduction to nutrient management.* 8th ed. Upper Saddle River (NJ): Pearson.
- Kabata-Pendias A. 2010. *Trace elements in soils and plants.* 3rd ed. (Google eBook). Boca Raton (FL): CRC Press.
- Kuo S, Mikkelsen DS. 1980. Kinetics of zinc desorption from soils. *Plant Soil.* 56:355–364.
- Lee JA, Wigner KA, Gregory JM. 1993. Drought, wind, and blowing dust on the Southern High Plains of the United States. *Phys Geogr.* 14:56–67.
- Liang J, Karamanos RE. 1993. DTPA-extractable Fe, Mn, Cu and Zn. In: Carter, MR, editor. *Soil sampling and methods of analysis.* Boca Raton (FL): CRC Press.
- Lindsay W, Norvell WA. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci Soc Am J.* 42:421–428.
- Ma YB, Uren NC. 1997. The effects of temperature, time and cycles of drying and rewetting on the extractability of zinc added to a calcareous soil. *Geoderma.* 75:89–97.
- Manouchehri N, Besancon S, Bermond A. 2006. Major and trace metal extraction from soil by EDTA: equilibrium and kinetic studies. *Anal Chim Acta.* 559:105–112.
- McLaren RG, Clucas LM. 2001. Fractionation of copper, nickel, and zinc in metal-spiked sewage sludge. *J Environ Qual.* 30:1968–1975.
- Mehlich A. 1984. Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. *Commun Soil Sci Plan.* 15:1409–1416.
- Mehta S, Fryar AE, Banner JL. 2000. Controls on the regional-scale salinization of the Ogallala aquifer, Southern High Plains, Texas, USA. *Appl Geochem.* 15:849–864.
- Najafi-Ghiri M, Ghasemi-Fasaei R, Farrokhnejad E. 2013. Factors affecting micronutrient availability in calcareous soils of Southern Iran. *Arid Land Res Manage.* 27:203–215.
- Nelson DW, Sommers LE. 1996. Total carbon, organic carbon, and organic matter. In: Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour PN, Tabatabai MA, Johnston CT, Sumner M, editors. *Methods of soil analysis. Part 3 chemical methods.* Madison (WI): Soil Science Society of America.
- Reyhaniabar A, Gilkes RJ. 2010. Kinetics of DTPA extraction of zinc from calcareous soils. *Geoderma.* 154:289–293.
- Sajwan KS, Lindsay WL. 1986. Effects of redox on zinc deficiency in paddy rice. *Soil Sci Soc Am J.* 50:1264–1269.
- Sharma BD, Arora H, Kumar R, Nayyar VK. 2004. Relationships between soil characteristics and total and DTPA-extractable micronutrients in Inceptisols of Punjab. *Commun Soil Sci Plan.* 35:799–818.
- Soil Survey Staff. 2014. *Kellogg soil survey laboratory methods manual.* Soil Survey Investigations Report No. 42, Version 5.0. (eds. R. Burt and Soil Survey Staff). U.S. Department of Agriculture, Natural Resources Conservation Service; [cited 2015 Jun 6]. Available from: www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/stelprdb1253871.pdf
- Sparks DL. 2003. *Environmental soil chemistry.* 2nd ed. San Diego (CA): Academic Press.
- Sparks DL, Page AL, Helmke A, Loeppert RH, Soltanpour PN, Tabatabai MA. 1996. *Methods of soil analysis. Part 3 – chemical methods.* Madison (WI): Soil Science Society of America.
- Sposito G. 2008. *The chemistry of soils.* 2nd ed. New York (NY): Oxford University Press.
- Sposito G, Lund LJ, Chang AC. 1982. Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. *Soil Sci Soc Am J.* 46:260–264.
- Stout JE. 2001. Dust and environment in the southern high plains of North America. *J Arid Environ.* 47:425–441.
- Tack FMG, Verloo MG. 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *Int J Environ Anal Chem.* 59:225–238.
- Udeigwe TK, Teboh JMP, Eze N, Stietiya MH, Kumar V, Hendrix J, Mascagni HJ, Ying T, Kandakji T. 2015. Implications of leading crop production practices on environmental quality and human health. *J Environ Manage.* 151:267–279.
- Udeigwe TK, Wang JJ, Zhang H. 2009. Effectiveness of bauxite residues in immobilizing contaminants in manure-amended soils. *Soil Sci.* 174:676–686.
- [USDA-NASS] United States Department of Agriculture-National Agriculture Statistics Services. 2014. *Cotton ginning 2013 summary;* [cited 2015 Dec 30]. Available from: <http://usda.mannlib.cornell.edu/usda/current/CottGinnSu/CottGinnSu-05-09-2014.pdf>.
- United States Environmental Protection Agency-Inductively Coupled Plasma (USEPA-ICP) Users Group. 1982. *Method 200.7;* [cited 2015 Mar 30]. Available from: <http://www.nmenv.state.nm.us/gwb/documents/DairyRegs/NOIAttachment9-Exhibits/3224Exhibits/3224-1.pdf>.
- Wu C, Luo Y, Zhang L. 2010. Variability of copper availability in paddy fields in relation to selected soil properties in southeast China. *Geoderma.* 156:200–206.