

Interactive comment on “Fixation kinetics of chelated and non-chelated zinc in semi-arid alkaline soils: Application to zinc management” by Theophilus K. Udeigwe et al.

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Response To Reviewers Comments

Anonymous Referee 1 Received and published: 31 March 2016 Comments on manuscript “Fixation kinetics of chelated and non-chelated zinc in semiarid alkaline soils: Application to zinc management”

The manuscript is evaluates the availability of Zn in semi-arid alkaline soils. The several analysis conducted on the soils allow the discussion of the kinetic effects in the Zn availability in soils as well as its relation with other micronutrients. The experiments developed can be of interest for readers of the Solid Earth; it fits with the journal scope

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and contributes significantly to the advance in the knowledge of Zn in soils. In general, the manuscript has been well distributed, the experiments well described and an adequate discussion is presented.

However, the manuscript is directly connected with a recently published paper (Solid Earth Discuss., 7, 2875–2902, 2015) in which the same methodological approach was performed to examine the fixation kinetics of chelated and non-chelated copper micronutrient in semi-arid alkaline soils. In both papers, exactly the same experiment is present: soil collecting, soils analysis, soil fertilization with a mixture of Fe, Mn, Zn, and Cu chelated (or non chelated). While in the published one the results for Cu concentrations after fertilization and correlations with other micronutrients are presented, in the current paper under review it is the Zn results and correlations. In fact it seems that only one experiment was performed and the results have been divided for the two manuscripts and maybe for two future ones on Mn and Fe. The text is frequently the same. From my opinion, it is the Editor who must decide if this way of results dissemination is valid. If this is a possible way of publication, I suggest, however to refer this paper to the previous one more clearly. In Line 85 this paper is cited but in a poor way. Moreover, I suggest other changes: - the soil properties have been presented as new results in Results section in Tables 1, 2, 3. Exactly the same values were presented in the previous paper. For this reason, the soil properties must be referred to the previous paper and not presented as new characterization.

We thank the reviewer for his views and suggestions.

This study is a part of a broad project on elucidating micronutrient fate in semi-arid alkaline soils. The manuscripts are different, the first focused on copper and this study is on zinc. Although, the soils are same and thus some background information on the study site may be similar. However, the major findings are completely different. The overlap in the two are only in basic soil properties which are primarily background information. However, the studies have totally different outcomes.

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We have therefore made some revisions and cited the first published work extensively where necessary. We have minimized the discussion of the basic soil characteristics (see section 3.1 Soil properties) which are similar and cited the first published work in its place. Thus, Table 1 is modified, and Tables 2 and 3 completely removed as a result and referenced made to the first published work.

See line 105 to 108 and section 3.1.

-In Table 5, the correlation with other metals is presented. In the previous one the correlation Cu/Zn was already presented. Thank you. This has been checked again and it is correct. Although the correlation Cu/Zn was presented in the first work, here the Zn/Cu correlation is needed to draw the needed comparison among the elements and between the systems (chelated and non-chelated). So, this is correct.

-Line 195-196: the comments are very general; the values are not according to the table. This has been taken care of with the revision early explained, where we cited the previous publications instead of discussing the soil properties again.

-Line 209-210: Rewrite the sentence. It is not clear. This sentence has been removed. There is no more need for it with the current revision.

-Line 237-238: The half-life of EDTA is possible not the main explanation for the decrease in Zn stability with EDTA in long times. Authors must also explore other metal competences such as Ca which is the main competitor for EDTA in alkaline-calcareous soils. Thank you! Reference to the effect of calcium on EDTA has been added to support this portion of the discussion (Line 232).

-Line 257-259: the comments are highly general considering the large interval range recorded in R2. Please, re-write. Thank you. This has been revised and average R2 used for the comparison instead of range (Line 249-250)

-Line 261-263: the relation Cu-Zn is presented. No reference is done here to the previous paper despite the same values of correlations have been found. The reason

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for reporting this has also been justified previously. Although the correlation Cu/Zn was presented in the first work, here the Zn/Cu correlation is needed to draw the needed comparison among the elements and between the systems (chelated and non-chelated).

-An important correlation has been found for Zn/Cu in non-chelated systems. Authors must discuss better this important fact and compare with the literature. An explanation has been added (Line 257-259). This important finding suggest that available Cu and Zn would tend to change at about the same magnitude in these soils as evidenced from the slope (0.82-1.00) and the highly significant R². However, we have not found a literature where these relationship has been evaluated from a similar approach for comparison, thus the significance in of this study.

-Line 283. Coefficient of determination is described as R². Please, check the correct nomenclature for R². This is rightfully used.

-The fixation kinetics for Zn in chelated systems has not been finally explained. The authors must deep into this fact and try to apply other models and cited literature with similar works. In conclusions it is mentioned that this papers contributes to understanding the Zn fixation chemistry in soils. However, a poor discussion has been done. Authors must correlated results with soil chemistry literature and try to explain which reactions are contributing to metal decrease: chelate dissociation, adsorption in soil materials such as clays, charges, precipitation, redox, etc. We appreciate this suggestion. However, the request of the reviewers is completely outside the scope of this work which is on understanding the fixation kinetics of Zn. Literature on the processes and mechanisms of zinc fixation were reviewed in our introduction. As mentioned in our conclusions, the reviewer's request, which is on the reaction mechanisms involved in zinc fixation in chelated and non-chelated systems of these semi-arid soils will be studied in the future research from this group.

Table 4. Authors kept the footnote referring Cu. This is referring Zn. Thank you so

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much for this. It has been corrected.

Table 5. A further explanation of the equation is needed. The value with statistics is not properly described (it must be indicated if R or pearsons P is presented). The slope is underline, specify this and reason. We have clearly specified the equation and statistics “R2” in the table. We have removed the underline to avoid the confusion. This was originally done to improve the visibility because we referenced the slope a lot in our discussion.

Anonymous Referee 2 Received and published: 17 April 2016 For the most part this is a well-done study. There is valuable information to add to the scientific literature concerning micronutrients in semi-arid soils.

However, I am very troubled by the apparent lack of ability to document level of variability in the work done to characterize the soil series used in this study, if at all possible this variability should be documented. In addition, it seems the authors would have a better paper if they combined this with their paper on Cu, also submitted to Solid Earth. Cover all the micronutrients at one time in one paper. I know this doesn't get the authors as many papers, but the one paper will likely be better cited than the separate papers because it will be more complete. Also, there is a large amount of overlap between the Cu and Zn paper that is not good. The authors are basically trying to publish the same data twice as two different papers. For this reason I recommend rejection of this paper, and combining the Cu and Zn data.

Firstly, the manuscripts are different, one focused on copper and the other on zinc. Although, the soils are same and thus some background information on the study site may be similar. However, the major findings are completely different. The overlap in the two are only in basic soil properties which are primarily background information. However, the studies have totally different outcomes.

We have therefore made some revisions and cited the first published work extensively where necessary. We have minimized the discussion of the basic soil characteristics

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(see section 3.1 Soil properties) and have cited the first published work in its place. Thus, Table 1 is modified, and Tables 2 and 3 completely removed as a result, and referenced made to the first published work.

Secondly, the manuscripts are intended to be published separately because previous effort made to integrate all the findings in one manuscript led to a densely packed work that was difficult to comprehend. Thus, the need to separate the data and publish our findings as two different publications that would complement each other. It was never our intention to publish the same data twice as two different papers in order to get many papers, as alleged.

Thank you

This manuscript needs a careful editing for English. The English is pretty good, but there are small issues scattered through the manuscript that distract from the overall reading. The first author is at Texas Tech, I suggest asking a native English speaking colleague to read through the manuscript and make suggestions. Thanks for the suggestion. We have taken time to edit the manuscript again

Lines 80-82 – Are there any publications in the literature, even extension publications, to back this statement about low levels of micronutrients in the agricultural soils of the Texas High Plains? A citation would significantly strengthen this statement. These are recent observations, not yet published. However, Bronson has documented this previously: Bronson, K. F., Trostle, C. L., Schubert, A. M., Booker, J. D. (2004). Leaf nutrients and yields of irrigated peanut in the Southern high plains: Influence of nitrogen, phosphorus, and zinc fertilizer. Communications in soil science and plant analysis, 35(7-8), 1095-1110.

Line 110 – “: :(15-30 cm) soils: : :” should be “: : :(15-30 cm) soil samples: : :” We don’t collect entire soils, we collect samples of soils. This has been corrected (Line 113 and 114). Thank you!

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Section 2.2 –Was there any replication of the samples used to characterize the soils, or was there just one run for each site and each depth? I know composited soil samples are common in soil fertility studies, but the way this was done doesn't give any feel for the variability in these soils, which is very important. There were surely lab replicates. However, no field replicate was needed for our study. We use composite samples from each field because we were not interested in within field variability. However, variability within the soil types (in terms of the properties) were examined.

On Table 1, for example, it can be seen that there is a fair amount of difference between the values obtained for OM, clay, and CaCO₃ in the three soil series. Is this a true difference, or an artifact of getting a single soil sample that isn't particularly representative? We don't know, because we don't have any measure of variability in the soils used for the study. These are believe to be true differences. Remember the composite samples were collected from a number of spots and mixed, given a representative sample for each field.

Whether or not there is a difference between these soils is an important question in this study. Do we see a lack of difference in micronutrient behavior in these three soils because they are similar, or in spite of the fact they are different? The inability to determine this is a major weakness of this study. The differences in soil properties among the soils were examined and mentioned (Section 3.1), however, there was no remarkable differences in micronutrient fixation pattern that we could be attributed to the differences among the soil properties.

Line 202 – In addition to Adriano, 2001 and Kabata-Pendias, 2010, I recommend citing Czarnecki and Düring, 2015 here. Thank you. This has been added (Line 197).

Line 255 – Some non-significant relationships were found in the non-chelated soils. This is acknowledged in Line 267, but that fact should be clear from the beginning. This statement has been corrected. The word “significantly” has been removed.

Table 1 – Measures of variability for these properties? This should be a table showing

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the soil properties and the differences. However this table has been revised and the soil properties contained only referenced in Udeigwe et al., 2016 to avoid duplication (Udeigwe, T. K., Eichmann, M. B., Menkiti, M. C., Kusi, N. Y. O. (2016). Examining the fixation kinetics of chelated and non-chelated copper and the applications to micronutrient management in semiarid alkaline soils. *Solid Earth*, 7, 311-321)

References Czarnecki, S., Düring, R.-A., 2015. Influence of long-term mineral fertilization on metal contents and properties of soil samples taken from different locations in Hesse, Germany. *SOIL* 1, 23-33. doi:10.5194/soil-1-23-2015. Thanks so much for this.

Interactive comment on *Solid Earth Discuss.*, doi:10.5194/se-2016-51, 2016.

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Response To Reviewers Comments**Anonymous Referee #1**

Received and published: 31 March 2016

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