SOIL Discuss., referee comment RC2
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Comment on soil-2020-81

Anonymous Referee #2

Referee comment on "The effect of soil properties on zinc lability and solubility in soils of Ethiopia— an isotopic dilution study" by Abdul W. Mossa et al., SOIL Discuss., https://doi.org/10.5194/soil-2020-81-RC2, 2021

General comments

The paper presents interesting research on zinc lability and solubility in Ethiopia. Understanding the behaviour of zinc in these soils is essential in combating zinc deficiency, which is an issue affecting a quarter of the population in Sub-Saharan Africa. The authors explain in detail the influence of soil properties on different measures of zinc lability and show that these properties are more important than the total zinc content. The conclusion is that soil acidity is by far the most dominant factor, and for some soils the organic matter content plays a role. This information is useful in designing soil management strategies to improve zinc availability. The manuscript does not have a clear multidisciplinary context compared to other articles in SOIL, nevertheless the results may be relevant for a broad international audience.

My overall impression is that this paper is very well written and contains a lot of relevant information. I have no comments on the introduction. A major shortcoming was found in the methods, where too little attention is paid to developing an adequate geochemical model. Next, I feel the results and discussion section is generally very interesting, but could benefit from better organization. My main concern here is that relatively little attention is paid to the explanation of the study's own results, as the paper regularly reads like a literature review without clear reference to what those citations mean for the interpretation of data. In addition, the introduction clearly states the problem of zinc deficiency, and as such the implications for soil management should be part of the discussion, instead of only a few sentences in the conclusion. Overall, this is a high-quality paper that with moderate revisions would be suitable for publication.

Specific comments

Title

The title suggests an isotopic dilution study, while ID is only part of the work. The importance of the study seems to be to explain the effect of soil properties, for which ID was part of the methods but not the sole or main method. It is recommended to include 'soil properties' in the title, and remove 'an isotopic dilution study'.

Methods

Line 72: what determined the time of oven drying between 24-48 hours, and did that have an influence on the results?

Please write in full the abbreviations the first time they are used (e.g. VWP, NPOC).

Some more attention should be given to the modelling using WHAM7, especially with respect to the models for Al, Fe and Mn oxides. What type of model is used and on which specific oxides is the parameterisation of the models based? What are the assumptions with respect to the specific surface area. The input should be described more precise e.g. line 139 "Inputs to the model included cation and anion concentrations...." Specify which cations and anions and whether inputs are solution concentrations or concentrations in the soil solid phase. Do the cations include Fe^{3+} and Al^{3+}? Tipping showed that these are important cations to consider because of their competition with other (trace) metals for binding to (dissolved) organic matter. In the case these cations were not measured their activities can be calculated from equilibrium with iron- and aluminium (hydr)oxide according to Tipping et al. 2002 (Geochimica et Cosmochimica Acta 66, 3211-3224)

A shortcoming of the study is the limited representativeness of the geochemical model for tropical (weathered) soils used to explain Zn lability and solubility. This stems from the assumptions made for the adsorptive constituents that are based on temperate soils, whereas the authors make it clear in the introduction that it is their ambition to study tropical soils, with the expectation that these will be different. This difference between tropical and temperate soils should then also be reflected in the model. The average fraction of humic substances was 36% for tropical soils modelled by Van Eynde et al. (2020): *Boron speciation and extractability in temperate and tropical soils: A multi-surface modeling approach* (Applied Geochemistry); this is notably different from the 50% used in the present study. In the study of van Eynde et al. it is also shown that the oxalate extractable Fe (non-crystalline oxides) is small compared to the dithionite extractable Fe (crystalline and non-crystalline) in such tropical soils. In the present study only oxalate extractable Fe is considered. Although the non-crystalline oxides have a much larger surface area than crystalline oxides, this may lead to an underestimation of the binding to iron oxides. Binding of metals to iron oxides is especially important at higher pH, which is the pH range for which the present study shows the highest overprediction of modelled soluble Zn. A positive point is the modelling of binding of Zn to Mn oxides which is usually not considered in multi-surface modelling studies for soils (see review Groenenberg and Lofts, 2014 Environ. Toxicol. Chem. 33, 2181–2196). The study shows that Zn binding to Mn-oxides may be highly relevant according to model predictions.

Results and Discussion

Line 170: indicate what could cause the discrepancy between observed values and those reported for contaminated and uncontaminated soils.

Line 172: indicate why it is relevant that concentrations were positively skewed

Figure 1: the added value of this figure in addition to Table 1 is unclear. Only two references are made to it (Line 172 and Line 183), and the skewedness of the data is not explained to be that relevant that it deserves a full figure. Additionally, inferences can be made about the skewedness by comparing the median and mean values in the min-max range as is done in Table 1. It is suggested to remove the figure.

Figure 2: it is unclear which label belongs to which line. PCA was also not explained in the statistics. It is felt that if the objective is to 'evaluate the correlation between soil variables' (Line 186) a correlation matrix is more intuitive than a PCA graph.

Line 209: please add a brief final sentence on the overall method assessment and validation step

Line 220-223: unclear why this is relevant. In general it is suggested to start with the most important explanations. It should be clearly explained why it is relevant to compare soils of the present study with urban or temperate agricultural soils when interpreting the pH effect.

Line 238-277: in the manuscript, this constitutes a one-page explanation of non-labile colloidal particles, leading to the conclusion that the correlation between Zn_E and pH is genuine. This text can be shortened significantly. In addition, this part is more of a literature review, with relatively detailed accounts of the results found in other studies. What is missing is the link between the literature and the results found in the present study. For example, in line 266 the paragraph ends with the notion that solutions were filtered to 0.22 um; the authors fail to state what this means for their work and their data.

Line 356-: In addition to the already mentioned possible explanations for overprediction also the presence of Zn-Al layered double hydroxides or Zn containing phyllosilicates could be considered (see already cited Bonten et al. 2008 and citations therein)

Conclusions

What is missing is a paragraph on the implications of the research for combating Zn deficiency. In the conclusion some 'tools' are mentioned, but this should be elaborated on at the end of the discussion. For example, it is concluded that it is soil properties rather than variation in total zinc that determines variability, but this is not translated in an overall conclusion on the conditions under which Zn deficiency occurs. A low solubility can still mean more Zn uptake if the total pool is larger, and vice versa.

Technical corrections

Line 14: either explain what 'major knowledge gaps' are meant, or more generally indicate that SSA soil types are understudied.

Line 76: comma or *and* after 'was determined'

Line 135: remove comma after 'any deviation'

Line 176: significant but weak positive correlation

Line 190: explain what is meant with 'react in opposite ways'

Line 206: 'but' = and

Line 224: 'changes' = differences

Line 235: start a new paragraph on non-labile particulate matter

Line 273: unclear what is meant with 'magnitude of the trend'

Line 282-283: unclear why this is important for the present study, should be explained

Line 302: the authors should make it clear that the pH-trend for Kd_{lab} contrasts the one found for Zn_E, instead of leaving it for the reader to infer.

Line 316: the 'p' looks like rho

Line 316: ‘some influence on metal adsorption strength would be expected’, this is vague and should be explained more clearly. In general, the remaining sentences of this paragraph should be elaborated on, to further clarify the pH-effect, and contain a brief conclusion.

Line 323: comma after ‘strength of adsorption’

Line 361-365: this can be shortened, as all cited studies conclude the same