

Second Responses to Referees: MS No.: soil-2020-81

Title: Zinc lability and solubility in soils of Ethiopia – an isotopic dilution study

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Thank you for your additional comments on our work.

Referee 2

The authors have addressed most comments and have made improvements of the original manuscript. As stated before, the manuscript contains much interesting data and findings. However, the major shortcoming in the development of geochemical models as expressed previously has, in my view, been insufficiently addressed.

The title, abstract and primary objectives do not mention a geochemical model. The focus thus far is on soil properties and isotopic dilution, and the main findings about Zn solubility (especially the pH effect) are based on correlation analysis.

Response: Thank you for your suggestion—we propose adding the following statements to the abstract and objectives respectively:

“A parametrised geochemical assemblage model (WHAM) was also employed to predict the solid phase fractionation of Zn in the soils under study, as an alternative to sequential chemical extractions.”

“to investigate the best of three possible input parameters defining reactive Zn in tropical soils (isotopically exchangeable, DTPA-extractable, total) when using a parameterised geochemical assemblage model to predict Zn solubility—assumed likely to be the principal driver for plant uptake”.

In the results, the last paragraph of 3.2.2 contains WHAM7 modelling, amongst others of the free Zn ion activity, which comes back in 3.5 (“Free Zn²⁺ activity in soil solution), but there the free Zn activity is shown to be pH-dependent based on simple correlation analysis. The section explicitly devoted to multi-surface modelling of soluble Zn (3.4) mainly evaluates the use of different inputs for geochemical models (ZnE, Zntot, ZnDTPA) in the prediction of Zn solubility. In contrast, in the conclusion the authors state “In this study combining (i) an isotopic dilution approach to determining reactive soil Zn (ZnE) and the relative strength of available Zn adsorption (K_d) with (ii) geochemical speciation modelling (WHAM7) provided useful insights into the intrinsic reactivity of Zn in SSA soils at a regional scale and revealed the key soil variables determining Zn solubility”. In short, the role and importance of the geochemical model in the study is thus unclear.

Overall, the above the impression that geochemical models were used (i) to understand the role of soil properties and reactive surface in Zn solubility and (ii) in the comparison of different assays of Zn status. For both purposes, adequate model development and description is crucial.

Response: For better readability, we suggest reorganising the result and discussion section in the revised manuscript such that a subsection (3.4) is devoted solely to discussing geochemical modelling results.

Particularly:

- Compared to the original submission, a somewhat more detailed description of the geochemical model has been added. Nevertheless, it seems to remain a ‘black-box’ approach with reference to a model and not to a publication where the ‘standard parameters’ could be found. As far as I know. the publication on the oxide models in WHAM is *Lofts and Tipping, An assemblage model for cation binding by natural particulate matter, Geochimica et Cosmochimica Acta*, Vol. 62, No. 15, pp. 2609–2625, 1998 and has never been updated. There is little justification of choices made about the model (WHAM7) or about the selection of reactive surfaces.

Response: Several geochemical models which predict metal speciation in aqueous systems and soils have been developed. The intent behind using a geochemical model in the current work was not to compare different geochemical models nor to attempt to re-parameterise the WHAM model specifically. Rather, the purpose was simply to test three established measurements of Zn availability as alternative inputs to an established model (WHAM7), to predict Zn concentration in the soil solution, utilizing a large dataset from tropical soils.

The model WHAM7 was chosen because it has a long development heritage, it is commercially available in a fully parameterised form, has a proven track record and is widely used. For example, a simple search on the Web of Science database using the key words “WHAM” and “soil”, between 2016 and 2020, yields 28 publications in which WHAM was used in a range of different scenarios. Thus, regarding the choice of reactive surfaces, we are obviously limited by the options that the model offers. However, we have acknowledged in the paper that there are potential reactive surfaces in calcareous soils that are not accounted for in WHAM which may help explain some trends in model fit observed.

- The authors rightfully acknowledge that the main weakness in geochemical models is the rough measurements of reactive surfaces that are used as input. I understand the choice of the authors to use the 50% humic substances assumption that ‘has been used extensively in the literature over a wide range of soils’. Nevertheless, as a general comment, this wide range of soils is hugely underrepresented by tropical soils. As such, it is felt that it would have been a valuable addition to the paper to evaluate what would happen with estimates (e.g. of Zn solubility) if actually measured humic substances values are used (such as in Van Eynde). After all, to improve our understanding of tropical soils (an ambition explicitly stated by the authors in the introduction), we need to build on other studies.

Response: We agree with the referee on the importance of full characterization of adsorption surfaces, including those associated with soil organic matter and all forms of oxides (Fe, Al, Mn) and aluminosilicate clay minerals. Ultimately this may be necessary to fully validate input variables for geochemical models applied to all soils. Unfortunately, such an undertaking was beyond the scope of this work which utilized 465 spatially co-ordinated tropical soils. Nevertheless, to investigate the importance of error in quantifying organic adsorption surface capacity, we ran the model assuming 36% of the soil organic C to be ‘active’, as suggested by Van Eynde, rather than 50% as utilized in previous studies. The result of these simulations are presented below in Fig. S1. The *change* in Zn_{Soln} was highly pH dependent and ranged from –4.8% to -39.8% with a maximum disparity at soil pH 5.5. The trend shown in Fig. S1 (below) reflects the fractionation shown in Fig. 7B of the manuscript where HA dominates the fractionation of Zn in this pH range and so any change in estimated HA concentration has the greatest effect on Zn solubility. The effect of the composition of soil organic matter on model performance was assessed using the residual mean square error (RMSE) between measured pZn_{Soln} and pZn_{Soln} predicted by WHAM7 using different Zn bioavailability estimates as input parameters. The results of these comparisons are presented in Table 1.

Table 1. Residual mean squared errors of measured pZn_{Soln} and predicted pZn_{Soln} by WHAM7 assuming 50% of SOC active and 36% of SOM active.

Input variable	RMSE (50 % of SOC assumed active)	RMSE (36 % of SOC assumed active)
Zn_{Tot}	2.63	2.70
Zn_{DTPA}	0.42	0.48
Zn_{Soln}	1.32	1.39

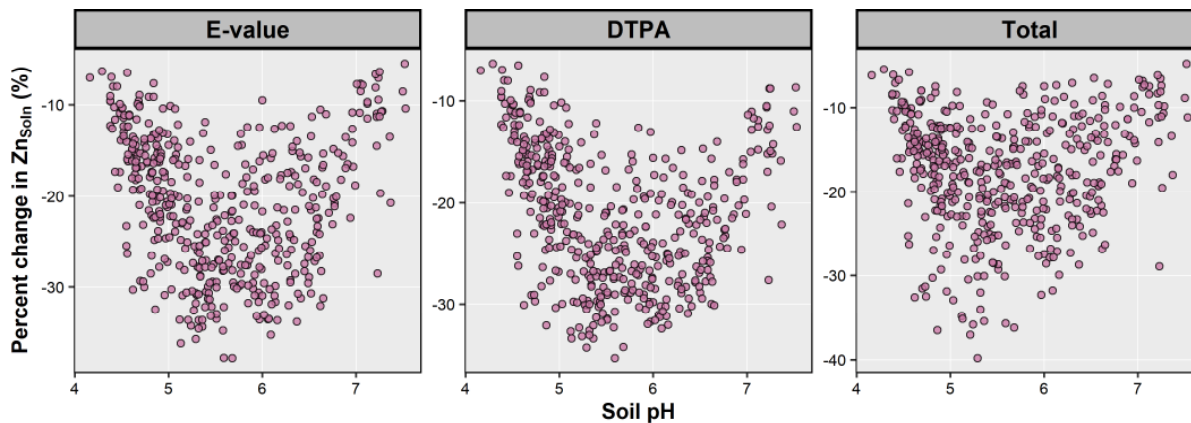


Figure S1. Relationship between soil pH and percent change in Zn_{Soln} predicted by WHAM7 when assuming only 36%, rather than 50%, of soil organic C is active. Zn_{Soln} was predicted by WHAM7 using isotopically exchangeable Zn, DTPA-extractable Zn, and total Zn concentration in soil as inputs.

We suggest adding Fig. S1 to the supplementary material and adding the following section to the revised manuscript:

“In common with previous studies, soil reactive organic matter was estimated as 50% of total soil organic C in all cases. However, in reality the composition and the reactivity of soil organic matter will differ between soils and there is currently uncertainty regarding the use of a universal value. Thus, for instance, Van Eynde et al., (2020) found that the average fraction of humic substances in 5 tropical soils was 36%. Consequently, there will be an associated error when relying on such assumptions in the absence of full characterization of soil organic matter in all soils. This is particularly important in the current study because while WHAM has been used and validated in several studies on temperate soils (Buekers et al., 2008; Izquierdo et al., 2013; Mao et al., 2017), to our knowledge, it has not been used on tropical soils. To test the effect of soil organic matter composition on model performance, we ran the model assuming 36% of soil organic C to be ‘active’ humic substances, as suggested by the data of Van Eynde et al., (2020). The results of these simulations are reported in Fig. S1 in the supplementary material. The change in Zn_{Soln} was pH dependent, ranged from –4.8% to –39.8% of the originally modelled value, and the maximum change occurred at soil c. pH 5.5. These results are relatively small changes considering that Zn_{Soln} covers over 4 orders of magnitude in the entire dataset”.

- My earlier comment on the importance of iron oxides (crystalline and non-crystalline) in metal binding at high pH (where overestimation of Zn solubility was found) was not addressed or incorporated in the discussion.

Response: Apologies for this omission. To test for potential effects of crystalline oxides on model performance, we ran the model using double the amount of Fe oxide estimated by oxalate extraction. This is probably an overestimate of Fe oxide adsorption capacity because the specific surface area of amorphous iron oxide may be 6x that of crystalline Fe oxide (Dijkstra et al., 2004). The ratio of crystalline to amorphous Fe oxide is clearly soil dependent but Van Eyndes et al., (2020) observed found that oxalate extractable Fe (amorphous) was smaller than dithionite extractable Fe (crystalline and amorphous) in tropical soils. Nevertheless doubling the Fe oxide content serves to test the sensitivity of the model to this variable. The results of these simulations are reported below in Fig. 2. The decrease in Zn_{Soln} was up to 24% and was highly pH dependent where the effect was negligible at soil pH below 5.5. The model performance was assessed using the residual mean square error (RMSE) between measured pZn_{Soln} and pZn_{Soln} predicted by WHAM7 using different bioavailability Zn estimates as inputs to WHAM. The results of these comparisons are presented in Table 2.

Table 2. Residual mean squared errors of measured pZn_{soln} and predicted pZn_{soln} by WHAM7 using measured amorphous Fe oxides and double the concentration of amorphous Fe oxides.

Input variable	RMSE (measured amorphous Fe oxides)	RMSE (double the concentration of measured amorphous Fe oxide)
Zn_{Tot}	2.63	2.60
Zn_{DTPA}	0.42	0.42
Zn_{Soln}	1.32	1.30

We suggest adding Fig S2 (see below) to the supplementary material and adding the following section to the revised manuscript:

“Both amorphous and crystalline Fe oxide are involved in Zn binding in soil. The specific surface area of the crystalline Fe oxide has been assumed to be 1/6 of that of the amorphous Fe oxide (Dijkstra et al., 2004). However, it was previously found that oxalate extractable Fe (amorphous) was smaller than dithionite extractable Fe (crystalline and amorphous) in tropical soils (Van Eynde et al., 2020). For comparison, model performance was tested using double the amount of amorphous oxides as inputs. The results of these comparisons are presented in Fig S2 in the supplementary material. When doubling the amount of particulate Fe oxide in WHAM7 inputs, there was on average 3.42%, 5.43%, and 2.56% decrease in predicted Zn_{soln} when using Zn_E , Zn_{DTPA} , and Zn_{Tot} as inputs respectively. However, the change was highly pH-dependent, and although the effect was negligible at soil pH < 5.5 (Fig. S2) there were much greater changes in the pH range 6 – 7 – up to just over 10% for Zn_{DTPA} model inputs.”

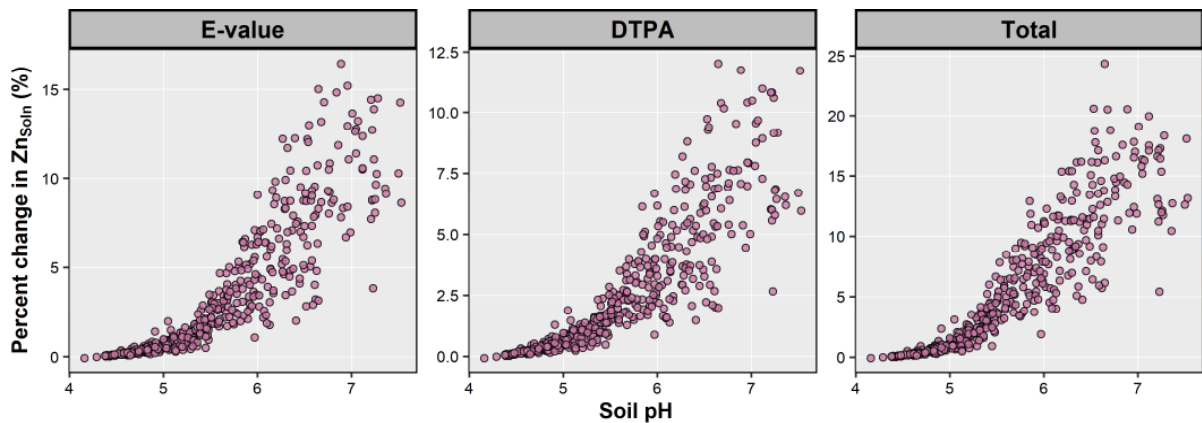


Figure S2. Relationship between soil pH and percent change in Zn concentration in soil solution, when assuming double the concentration of measured amorphous Fe oxide. Zinc concentration in soil solution was predicted using WHAM7 using isotopically exchangeable Zn, DTPA-extractable Zn, and total Zn.

- Mn oxides: regarding the parameterisation of the Mn-oxide model in WHAM7, Lofts and Tipping (1998) wrote “Application of the SCM model was made difficult by the relatively sparse adsorption data, uncertainty with regard to oxide properties, and variability among results from different laboratories” They found pK values for the binding constant for Zn ranging from 0.6 to 4.2 (Table 3). Because of the importance found for Mn-oxide in the binding of Zn in the present manuscript it would be good to address somehow the uncertainty of this model.

Response: We agree with the referee on this point. However, as we stated above, our objective in using the geochemical model was to test the capability of WHAM7, using its default parameters, in predicting Zn solubility.

As such, we think it is beyond the scope of this manuscript to attempt to test for different binding constants for Zn onto Mn oxide. As an alternative we suggest adding the following section to the revised manuscript:

“In the current study, Mn oxides appear to be an important binding phase for Zn. The binding constant, pK_{MH} for Zn onto Mn oxide in WHAM7 is 1.6. However, Lofts and Tipping, (1998) found that measured binding constants for Zn adsorption by Mn oxide ranged from 0.6 – 4.2. They attributed the difficulty in modelling adsorption onto Mn oxides to sparse adsorption data, uncertainty in Mn oxide properties, and variation among results from experimental data. Therefore, the results of modelling Zn adsorption onto Mn oxides, as predicted by WHAM7, should be viewed with caution.”

In conclusion, I suggest the authors to pay more attention to applying an adequate geochemical model and clarify the role of such a model in relation to the study objectives.

Response: We hope that by our responses and proposed changes to the manuscript, the referee will be satisfied that we have clarified the objective of using geochemical modelling in the current study.

Technical comments:

In the previous review, I suggested starting a new paragraph at Line 235; this should be after the sentence “In the calculation of...”, not before, because it clearly relates to the previous sentence. In general, in the revised manuscript little attention was paid to improved organizing of the discussion as suggested in the first review. This does not affect the scientific quality of the text, but could have improved readability, especially for a more general audience as targeted with the SOIL journal.

Response: We have re organised the results and discussion for better readability as suggested by the referee such that a subsection (3.4) is devoted solely to discussing geochemical modelling results.

The start of a new paragraph has been corrected in the revised manuscript.

Line 73 says "Fig. q" and does not have a closing bracket.

Response: Thank you—this has been corrected.