

Interactive comment on “Isotopic offset between unconfined water and water adsorbed to organic matter in equilibrium” by Guo Chen et al.

Anonymous Referee #1

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REFeree COMMENT-DISCUSSION

Isotopic offset between unconfined water and water adsorbed to organic matter in equilibrium

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General comments

In this work, Chen et al. present an experimental study aimed to quantify isotopic fractionation in water adsorbed to organic matter. The work is timely, particularly considering the increasing interest on understanding isotopic fractionation of water within the soil (see e.g. Tang Feng 2001; Brooks et al. 2010). In previous studies, the role

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of mineral adsorption and hydration have been explored. However, till now a study on the effect of water adsorption by organic matter was lacking, despite this may also play a significant role in soil processes. In this regard, the present work provides robust experimental evidence of a process with strong implications in different fields, from surface hydrology to the study of plant water uptake.

Specific comments

Experiments

The methodology of the experiments is generally well described. My main concern is about the calculation of the solid:water ratio. Is it the apparent volume, as typically done for soils? Then, to what extent the porosity of the material could affect the results? For example, depending on how we handle the medical cotton, we can easily modify its volume. Would this change in "solid volume" affect the relationship in the same way as a change in hydration?.

The experiments describe the effect of water-vapour adsorption, but I wonder whether these results could be extrapolable to adsorption processes in the liquid phase, e.g. along the apoplastic water transport in plants. If this were the case, adsorption might explain the fractionation of water between source and xylem water that has been described for some xerophytic and halophytic species (see e.g. Ellsworth Williams 2007). A definitive mechanistic explanation for this process is still lacking and, interestingly, the effect is significant for hydrogen, but not for oxygen. Although right now rather speculative, this topic might deserve consideration for future work.

Application case

This section is particularly relevant, as a first attempt to validate the findings of the laboratory experiments. However, the way the data is presented could be improved, and the results deserve more attention in the discussion section.

Firstly, I would expand the methods section, describing the sampling protocol and,

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in particular, stating clearly that these values correspond to distilled water from the original soil sampling (i.e. nothing to do with the equilibration experiments).

The authors mention that they did not consider sand for their volume calculations, however, as for the rest of materials, they did not explain how they actually determined the ratio solid:water volume. Is it the apparent volume (i.e. including pores), or an estimate of the solid volume?. In the second case, how was this calculated/estimated? The methodology is likely to be based on standard techniques in soil science, but it is worth to mention them explicitly, particularly to help other researchers to validate the models with their own field data.

On the other hand, the discussion of the application case could be expanded by considering whether the observed relationship can be used to correct field data, and under which conditions. For example, it is worth to discuss why the upper soil seems to fit better with the solid:water ratio than the 20 cm layer. Potentially, this could be related to differences in organic matter content: was this actually the case? On the other hand, the authors apparently pooled together organic matter with clay as "porous" material in their calculations. However, if clay and organic matter do not behave in the same way, this might explain the differences between upper and lower soil layers. Since the soils tested have about 30% of clay, I would try to compare these results with the expected effects of clay minerals, e.g. as in Meissner et al. (2013).

Technical corrections

The experiments were designed to test the effect of water-vapour capillary absorption, Adding "vapour" (...water vapour adsorbed...) to the title may help the reader to quickly understand the experimental setup.

Section 2.8 Modelling, and Figures 2-4. In the modelling section, the authors included in the equations the water:solid ratios, whereas in the figures the ratio solid:water is used. I guess that for most readers the water:solid ratio would be more intuitive, so I would suggest to use it also in the figures. Similarly I would replace the term "enrich-

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ment" by "offset" or "deviation", which is neutral.

The way the data is presented in Fig.6 is somewhat inconsistent: whereas individual winter values are represented as symbols, the rest of data is presented indirectly with the fitted regression line. I would suggest to present all the data in the same form, ideally as individual dots with their corresponding regression line.

References

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