

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

Anonymous Referee #2

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Review comments on:

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

by: Guo Chen, Karl Auerswald, Hans Schnyder

General Comments:

This manuscript describes the results of a series of water vapor-adsorbed water experiments conducted to discern isotope fractionation effects related to the surface-water interface. The authors develop a two-compartment model to describe the observations. The results are fairly significant in that they seem to be relevant to a wide range of situations where there is a high soil-water ratio (i.e. soils and vadose sediments).

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My main comments are that the authors spend most of the discussion on refuting other explanations for these effects (which is good), but they do not spend much time discussing why these effects are relevant and in what instances. I think the discussion of the natural test case of soils needs to be better discussed and “rounded out” to include how these findings may be used in practice (i.e. What is the use of this effect in casein or flour?). In the abstract, “major implications” are claimed, but they are not ever really discussed. For example, could this effect explain observations of isotopic differences between mobile and immobile water in soils (i.e. Brooks et al., 2010, NatureGeosci, DOI: 10.1038/NCEO722)?

The figures could be improved by denoting each by a specific identifier (e.g. “A” or “B” etc). Figure 6 is relatively unclear to me, and could be improved by a more informative caption. The use of “enrichment” to describe the isotope effect throughout is problematic. Enrichment is used when the isotope effect is both positive and negative. I suggest a more neutral term that is also more descriptive, such as “positive (or negative) isotope effect” to describe the direction of change.

Specific comments by line number:

1. Needs a more specific, or informative title.
13. Avoid the term enrichment. The δ values of the water either got higher or lower, or remain unchanged.
14. Define significant
26. modify “discrimination” to something more descriptive and specific to this paper.
31. “Such fractionation can be affected by ion hydration.” Needs revising and a reference to support it.
36. “Additionally, adsorption, may cause an energetic difference between water molecules at the surface of solids and the bulk water molecules.” – Needs a reference.

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51. Please define “silage”.

54. Please define “casein powder”.

54. What kind (grain type, i.e. wheat?) of flour?

69 – 70. Please briefly define “fibric” and “hemic” rather than sending the reader somewhere else to find a definition that is important to understanding this paper.

78. Why were these materials “slightly dried” before the experiment?

79 -80. How do you know these constituent amounts? Did you do an analysis for this?

80. Why was casein and flour only dried at 50C for 6 hr rather than at 100C and overnight?

99 – 100. Was there condensation inside the pump? How do you know?

104. Was there any evaporative enrichment on the water dish after 100 hr of evaporation?

136. What is OLS?

163. “MIBA Protocol” doesn’t mean anything to me. Again, please briefly describe your methods and definitions without making the reader go look somewhere else to understand what you did.

168 “Further, the winter data, effects of soil evaporation from the vegetation covered soil, can be excluded.” Please justify and explain why you make this assumption.

171-172. “and sand grains usually are coated by clay, sequioxides, organic matter and biofilms and do not directly interact with water” This seems problematic: If the sand grains are coated with a fractionating substance, how can you neglect them in your analysis? Please address this.

184. Again, define “significantly”.

200-201. “The water content of oven dried silage did not reach again the same water content as fresh silage but was significantly lower ($81 \% \pm 13 \%$).” This seems important, please address this result.

216-222. Please expand this to include exactly how you calculated the Raleigh fractionation line in Fig. 5.

220-222. “Additionally, an unrealistically small fraction of water would have to be extracted (far below 0.8) to cause the same enrichment of 2 H as observed for most of the samples.” Please explain this more.

227: How where the evaporation numbers calculated?

284-289. I do not understand how this explanation rules out exchange of hydrogen and oxygen exchange.

301. Again, you need to explain terms that you invoke, i.e. what is “energy delocalization phenomenon”?

305-311. Oerter et al., 2014 (J. Hydrology) discussed possible reasons for these effects near clay surfaces in some detail. That work should be referenced here.

316. What is the volume ratio of the inner perturbed water to the total milk water? I assume small, so why would it show up in bulk water extractions?

323-331. In the abstract you claim “major implications” for these results but you do not really discuss any. What are some of the bigger implications of these results?

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