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 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 calculation of solid: water ratio is based on the solid volume, which is not the apparent volume. The porosity of the material will not affect this ratio. To make it clearer to the readers, we emphasize that the volume calculation has nothing to do with bulk volume:

"The solid volume (exclusive voids) can be calculated by knowing the weight and the particle density of the organic matters (casein: 1.43 g/cm^3 (Paul and Raj, 1997); silage, hay, litter, filter paper, cotton and flour: 1.5 g/cm^3 (Yoshida, et al., 2006))."

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.

We added the discussion about this:

"The surface effect may also play a role in the fractionation between source water and xylem water that has been described for some xerophytic and halophytic species (e.g. Ellsworth and Williams 2007) for which an explanation is presently missing."

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, 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).

We expand the methods section and showed our aims of the soil sampling in grassland:

"Soil at 7 cm and 20 cm depths and rain water were sampled at the grassland in Grünschwaige Experimental Station, Germany (48°23'N, 11°50'E, pasture #8 in Schnyder et al. (2006); 8.3 % organic matter, 30 % clay, 22 % sand) at biweekly intervals during the growing season (April to November) from 2006 to 2012 and at weekly intervals during the winter season (October to February) in 2015/2016. Soil sampling was always carried out on dry days at midday (between 11 a.m. and 16 p.m.). Two replicates of soil samples were collected on each sampling date. The data were used (i) to examine if there was an offset between soil water and rain water and (ii) whether the offset can be corrected by accounting for the solid:water ratio according to our model. In order to exclude that the offset is caused by soil evaporation, we only use winter season data. During the winter season, evaporation demand was low (average actual evaporation 0.5 mm/d while average precipitation was 1.9 mm/d; German Weather Service, 2016) and evaporation demand should be entirely met by transpiration and intercepted water due to the complete grass cover. Growing season data are only shown for comparison."

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.

The volume of solids, in general, was calculated excluding pores. The volumetric solid:water ratio of soil was estimated by the weight and solid density of the organic matter and minerals without sand. We added the calculation of volumetric solid:water:

"We had developed the relation between the volumetric solid:water ratio and the isotopic offset only for organic materials. These materials differed from the soil in so far as they did not contain minerals. Especially for sand it can be expected that it practically does not absorb water due to its small surface area. Hence, we considered the sand to be inert and did not consider it in the volumetric solid:water ratio, which in consequence was calculated from (volume of dry soil excluding sand) / soil moisture volume. The volume of dry soil excluding sand was calculated by dividing its dry weight by particle density of the organic and mineral components (1.5 g/cm^3 and 2.65 g/cm^3, respectively; Chesworth, 2008)."

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?

There was a small difference in organic matter content between both depths (the soil was arable about 10 yr before sampling) but we do not expand on this because we do not use this information.

We modified the results part:

"The deviation between the winter season data and the local meteoric water line correlated significantly ($p < 0.001$) with the solid:water ratio for 7 cm depth but not for 20 cm depth, which varied less in water content. For both depths, the data moved closer to the local meteoric water line when the influence of confined water was removed by applying the general regression with solid:water ratio from Fig. 2 (Fig. 6b). The mean deviation for $^{2/1}$H changed from -8.1 ‰ to 1.0 ‰ for both depths due to this correction."

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).

Meissner et al. used a different experimental setup, in which they did not equilibrate sample water with unconfined water but they compared extracted water with the water added. With this approach they measured the influence of exchange on the isotopic composition of the extracted water. This is a different process than in our case. Hence we did not compare with the results by Meissner et al. (2013). But we compared our results with the results by Oerter et al. (2014):

"In our experiments we had only examined organic materials while the soil in our application case also contained minerals. Given the "paradoxical effect" (Drost-Hansen, 1978) and that we had not found any effect of the nature of the organic materials on the surface effect, the simplest assumption was that there is also no large difference between organic and mineral surfaces regarding the isotope effect. This seemed reasonable because pure clay with 30 % water content (equivalent to 0.8 solid:water content) as used by Oerter et al. (2014) created -0.4 ‰ oxygen isotopic fractionation on average. This was close to the predicted apparent isotopic fractionation (-0.7 ‰) for the same solid:water ratio for organic materials. Oerter et al. (2014), however, also manipulated the composition of the solutes, which are known to affect fractionation and which do not allow direct comparison. "

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.

Actually "vapour adsorption" is not appropriate because most of our materials contained quite a lot of liquid water. We only used a saturated atmosphere for the exchange between unconfined water and material water in order to be able to measure both separately. To improve the title, we changed it:

"^{2}H and ^{18}O depletion of water close to organic surfaces".

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.

Yes, there were inconsistences between the figures and equation in terms of solid:water ratio. It should always read "solid:water ratio".

We agree that the water:solid ratio is much more common but our prediction was that ε_a should be related linearly to the volumetric solid:water ratio for the total adsorbed water. A linear equation is easier to fit (e.g., by linear regression) and it would be difficult for the reader so see whether the data really follow an inverse relation and not a deviating curvilinear relationship while it is rather easy to judge a linear relationship.

Similarly I would replace the term "enrichment" by "offset" or "deviation", which is neutral.

We replaced the term "enrichment" by "isotopic fractionation" throughout the manuscript according to your suggestion; we follow strictly Coplen (2011) now.

Reference: Coplen, T. B.: Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results, Rapid Commun. Mass Spectrom., 25, 2538-2560, doi: 10.1002/rcm.5129, 2011.

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.

We made it more consistent: all the values were shown as markers in this figure. However, the summer values (which previously were shown only as lines) are small markers because our arguments are based on the winter data and the summer data a just shown for comparison. And we do not present all regressions in the figure (they would be hard to distinguish because they overlap).