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Interactive comment on "Validation of a coupled $\delta^2H_{n-alkane}$-$\delta^{18}O_{sugar}$ paleohygrometer approach based on a climate chamber experiment" *by* Johannes Hepp et al.

Anonymous Referee #1

Received and published: 21 November 2019

BG-2019-427

Dear Johannes Hepp and co-authors,

I have to say that I really like you combined water isotope method for reconstructing source water isotope values and relative humidity. I found this manuscript extremely difficult to read, however. It is quite complex and difficult to keep track of all the different measured and modeled parameters and the writing and structure doesn't make this easier. I'll give a few examples of this in the more detailed comments. I do think if you significantly clean up the manuscript structure and writing issues it might be a worthwhile contribution to Biogeosciences, as is it is a bit difficult to judge. I do have

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a few, more general, comments. You have the tendency to position your combined method opposite to the n-alkane based reconstructions, by writing things like “However, a direct reconstruction of the isotopic composition of paleoprecipitation based on δ2Hn-alkane alone can be challenging due to the overprint of the source water isotopic signal by leaf-water enrichment”. The thing is the same holds true for δ18Ocellulose/sugars , so this is not necessarily a “bad” thing of the n-alkane method, in fact for reconstructing RH it is a good thing there is leaf-water enrichment, otherwise there would be nothing to reconstruct. Personally, I think all methods/proxies have their issues and we need to know what they are so we can work with them. Measuring both hydrogen and oxygen isotopes has its advantages, I can see that, not only do you get duplication, the combination of the two opens up new possibilities as well. For this you basically work back to the global meteoric waterline, is that always the most appropriate meteoric waterline to use? As far as I know local meteoric waterlines can differ quite a bit from the global, right? And also with the use as paleo proxy, meteoric waterlines might not be constant over time, glacial/interglacial changes for instance? Would that complicate that the use of your proxy and how? Do the field studies look at global or local meteoric waterlines, for instance? My last question deals with exchangeable oxygen as mentioned on page 11, “The relatively uniform fractionation is explained via the isotope exchange between the carbonyl oxygens of the organic molecules and the surrounding water (cf. Schmidt et al., 2001)”. You seem to suggest this might play a role in your sample set, right? But your samples are from 2001, so what would be the water is exchanged with, the water from the experimental set-up (leaf or other), from the freezer it was stored in or the lab they were analyzed in? Or perhaps oxygen form the organic solvents used? How would this affect your method, if at all, and calculating back to the global meteoric waterline, for instance?

Detailed comments:

Line 54: the leaf water data has been published already right? In Mayr 2002, so what is new here? The modeling? Line 55-56 and throughout the manuscript: I find the use

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of the more simplified or the less simplified C-G model very confusing. In the abstract it is even a bit meaningless since the reader has no idea what you mean. Perhaps you can give them a different name? First paragraph of the introduction: Be careful with taking down the n-alkane method, you need this leaf water enrichment of both H and O for your reconstructions. At the end of this paragraph I expect how your method will solve these issues, but it is not there. Second paragraph of the introduction: I think there are publications on isotope fractionation during water uptake through the roots, use them. There is also information on soil enrichment due to evaporation, it might have been discarded as major factor in most cases, but still interesting to mention, I think. Line 104: It is known to not be constant! You need to address this at least a little. 2.1: What about the return flow of enriched leaf water into the stems? How might that affect your measurements? You measured both xylem and phloem and called it xylem. Line 170: high temperature conversion (HT-EA-irMS) Line 179/200: use ‰ and not per mil. Line 181: strange definition of the delta notation. Line 258: less simplified results? The results of the less simplified (more complex or more correct) C-G model? Line 299: this is a bit worrying, the low number of samples per plant species prohibits a robust interpretation. . ... Line 328: so fractionation is not stable. . . introduce this in the introduction. . . Line 338: Epsilonbio is large and not constant and one of the main reasons for this NADPH and the sources of H for NADPH and the pathways by which NADP+ is reduced to NADPH, the enzymes involved etc. etc. It is not just another additional complicating factor. Line 359: What is this unenriched source water? Source water as in “precipitation” or in the experiment the big tank of water sourcing everything? Or source water as in the source for biosynthesis, so water in the leaf that has not been enriched by evaporation? Wouldn’t that mix or is it compartmentalized? How does what water end up where, this is confusing. Line 370: Now it is even depleted source water contributing to local synthesis water? How did it get depleted or is it depleted relative to the enriched leaf water? The same as the non-enriched source water? And the source is in this case the source for biosynthesis? Righ? Line 384: I thought I read -152 earlier in the manuscript as average? Line 403: This range from -

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192 to -133 was for Epsilonn-alkane-leaf water on the previous page? So do you mean Epsilonxylem water-leaf water here? Same for line 418? Already difficult to keep track of everything. Line 418: NADPH, photosynthesis, pentose phosphate pathway, etc. etc. etc.... Line 428-429: Oh, ok.... See above. Line 478: despite without? Which can be expected from literature? The latter definitely needs references, but I lost track of the meaning of this sentence. Line 484-485: an overestimation of models? Of the quality of the models, the outcome of the models? Line 488: There it is back diffusion of enriched waters? Did that affect your stem water measurements? Line 490-491: difficult to understand, there is no obvious reason for it? Line 494-495: measured values based on the less simplified model? Are they measured or modeled? The more complex or more correct model... Line 499-502: I am lost here. The more simplified models are still more accurate, despite the less simplified models do not reflect well the range of the measured SIel. Much better matches are found for the less simplified LEL slopes.... So the less simplified models are both worse and better? It's unclear to me, so please try to rewrite in way that is easier to understand. Line 535: the overlapping notches are a graphical representation of the lack of a statistical difference, right? ID so, don't use "with regard", but something like as illustrated by or so. Line 566: ...., can be explained as for the leaf water based application. Again I am lost here.

Again, I am always in favor of new proxies being developed and this an interesting development. I do however think that the manuscript as is will not do this new proxy any favors. This manuscript could benefit greatly from some restructuring and rewriting. The data deserves that.

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