

Interactive comment on “A dual-biomarker approach for quantification of changes in relative humidity from sedimentary lipid D / H ratios” by Oliver Rach et al.

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General Comments

The authors present a paleoclimate record from laminated sediments. They extract a dual hydrogen isotope record from two homologues of n-alkanes, each thought to be derived from aquatic algal production and terrestrial plant production, respectively. The attempt is to move beyond qualitative interpretations to develop quantitative interpretations of relative humidity. The approach is reasoned, the climate result important and the manuscript should be suitable for publication in CP after appropriate revisions. The manuscript is generally well written, although reviewer 1 has raised extensive comments about climatic interpretations and Ebio interpretations including the question of

why no modern calibration was attempted as part of proof-of-concept. I will not repeat any of these comments but will confine my review to raising a technical but substantive issue that undermines the quantitative claims at present, by introducing non-trivial arithmetic errors. If the authors revise their approach with the correct arithmetic formulations, the approach will be a quantitatively robust contribution. In my opinion this fundamental revision of the calculations is required before further consideration for publication. Without such correction, the introduction of non-trivial arithmetic errors represent an impediment to accurate climatic interpretations using a widely-used paleohydrological proxy.

Specific Comments

Line 74 “1:1” represents a misunderstanding of the mathematical implications of the relative isotope terms. A 1:1 line would not be expected for a fixed fractionation. Please review fractionation terms as indicated in Section 3.1 of Sessions and Hayes (2005). For the slope $y = mx + c$, $y = \alpha x + \epsilon$, where $\epsilon = \alpha - 1$. The difference term approximation is acceptable when α is between 0.95 to 1.05 as is often the case for carbon or oxygen but is inappropriate for hydrogen, when values of α may be 0.8 to 0.9 for many plants.

Similarly, equations 1-4 are not in the correct form, they are combined as though they were difference terms, when this is not appropriate for the relative calculations implicit in ϵ terms. Even if the results are trivially different (which they appear not be), this approximation is not advisable because it builds misunderstanding that is likely to propagate through the literature.

Equations of a similar form have been published for oxygen isotope considerations. The error introduced is trivial for the smaller fractionations associated with the smaller relative mass difference between ^{16}O and ^{18}O (Kahmen et al., 2011), but it matters when that approach is extended to ^1H and ^2H where the relative mass difference is 8-times higher and the fractionations commensurately larger. Admittedly the algebra will

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be considerable, but the formulation could be provided in a spreadsheet rather than as equations within the text. The authors must at minimum account for the uncertainties introduced by the mathematical approximations, but ideally they will revise their equations accordingly, given the magnitude of errors introduced are non-trivial for their RH interpretations.

Technical Corrections

I have performed some simple calculations with example input data to illustrate the magnitude of the arithmetic errors introduced by the incorrect formulation based on difference terms in Eqns. 1-4. I also illustrate that the 1:1 line is not the expected result of a fixed fractionation. The output is provided here (Figure 1) and the Excel file supplied as Appendix.

References

Kahmen, A., Sachse, D., Arndt, S.K., Tu, K.P., Farrington, H., Vitousek, P.M. and Dawson, T.E. (2011) Cellulose delta O-18 is an index of leaf-to-air vapor pressure difference (VPD) in tropical plants. *Proc. Natl. Acad. Sci. U. S. A.* 108, 1981-1986.

Sessions, A.L. and Hayes, J.M. (2005) Calculation of hydrogen isotopic fractionations in biogeochemical systems. *Geochimica Et Cosmochimica Acta* 69, 593-597.

Please also note the supplement to this comment:

<http://www.clim-past-discuss.net/cp-2017-7/cp-2017-7-RC2-supplement.zip>

Interactive comment on *Clim. Past Discuss.*, doi:10.5194/cp-2017-7, 2017.

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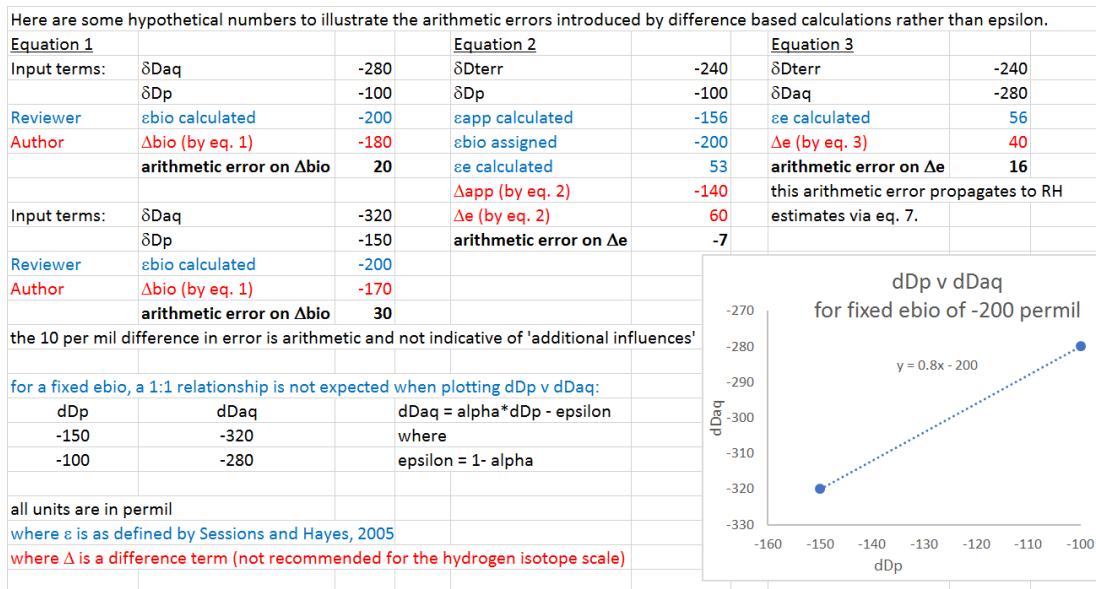


Fig. 1. Reviewer demonstrations of introduced errors by the difference approach

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