

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

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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 alpha is between 0.95 to 1.05 as is often the case for carbon or oxygen but is inappropriate for hydrogen, when values of alpha 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 epsilon 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 16O and 18O (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

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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Equation 1			Equation 2		Equation 3			
Input terms:	δDaq	-280	δDterr	-240	δDterr	-240		
	δDp	-100	δDp	-100	δDaq	-280		
Reviewer	εbio calculated	-200	eapp calculated	-156	εe calculated	56		
Author	∆bio (by eq. 1)	-180	εbio assigned	-200	∆e (by eq. 3)	40		
	arithmetic error on Δ bio	20	se calculated	53	arithmetic error on Δe	16		
			∆app (by eq. 2)	-140	this arithmetic error pro	opagates to RH		
Input terms: 8	δDaq	-320	∆e (by eq. 2)	60	estimates via eq. 7.			
	δDp	-150	arithmetic error on Δe	-7				
Reviewer	εbio calculated	-200						
Author	∆bio (by eq. 1)	-170			dDp v dDaq -270 for fixed ebio of -200 permil			
	arithmetic error on ∆bio	30		-270				
the 10 per mil	difference in error is arithme	tic and n	ot indicative of 'additional influ	ences' -280	n			
					y = 0.8x -	200		
for a fixed ebio, a 1:1 relationship is not expected when plotting dDp v dDaq:				-290	-290			
dDp	dDaq	d	Daq = alpha*dDp - epsilon	a = alpha*dDp - epsilon				
-150	-320	w	here	qt				
-100	-280	er	psilon = 1- alpha	-310	.10			
				-320)			
all units are in	permil							
where ε is as d	lefined by Sessions and Haye	s, 2005		-330	160 160 140 120	120 110 100		
and a set of the set of the	fference term (net recent	nded for	the hudresen isstens coole)		-100 -150 -140 -150	-120 -110 -100		

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