

Interactive comment on “Modern isotope hydrology and controls on δ D of plant leaf waxes at Lake El’gygytgyn, NE Russia” by K. M. K. Wilkie et al.

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The present study provides a detailed assessment of isotope hydrology and the hydrogen isotopic composition of n-alkanoic acids from sediments and catchment vegetation of Lake El’gygytgyn in NE Russia. The authors present this analysis with the aim of understanding the factors controlling sedimentary lipid distributions and their hydrogen isotopic composition. This detailed work can be used as a tool to interpret downcore changes in terms of paleohydrological changes. As such, the study is quite unique, as it aims to understand possible sources of these lipid biomarkers into lake sediments, as well as to clarify the possible water sources used by plants from within the lake

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catchment. Furthermore, it is one of a few studies investigating the modern controls of the hydrogen isotopic composition of n-alkanoic acids. In general the study presents a comprehensive sampling scheme, uses state-of-the art methods and is well written and structured. The dataset presented is unique and will be of great interest to for organic geochemists looking to apply n-alkanoic acid D/H ratios for paleoclimatic questions.

There a few minor issues to be dealt with, regarding the explanation of standard handling for compound-specific stable isotope analysis and some adjustments to the cited references (not always the cited references are applicable for the statements to be backed up). In my view there are also two major issues, which deals with data interpretation and how the results from the current study are put in context with other studies from the field. In a revision the authors should consider these issues and modify the data discussion accordingly.

Major issues: 1. n-alkanes vs n-alkanoic acids: The major part of the literature on the factors controlling leaf wax dD values is on n-alkanes, with only a few studies having investigated n-alkanoic acids. Despite overall similarities, these few studies (Hou et al. 2007; Huang et al. 2004) however suggest, that dD values of both groups of lipids do not record the same signal, i.e. correlation coefficients between these compound classes are significantly less than among compound classes. For example, based on the biosynthetic origin of n-alkanoic acids it is expected that they are enriched in D compared to n-alkanes from the same source by about $25\% \pm 16\%$ (see Chikaraishi & Naraoka, 2007) and also Sachse et al., 2012. Also differences in the timing (Jetter & Schäffer, 2001) and location of n-alkane and n-alkanoic acid biosynthesis in one leaf (with the consequence that for example different source waters are sampled by the plant or different amounts of leaf water evaporative enrichment are recorded by the different compounds) may account for the observed differences, but very little is known. From that viewpoint, the current study is crucial, as it specifically investigates the controls of n-alkanoic acid dD values, as an increasing number of paleoclimate studies make use of this compound class. I suggest to state this as one of the novel aspects

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of the study more clearly. But this also requires to put the current data in perspective with previously published alkane as well as alkanolic acid data, as the absolute values cannot be directly compared between n-alkanes and n-alkanoic acids.

2. constant net fractionation: I also recommend to restrain from suggesting a constant apparent fractionation for the application in paleoenvironmental reconstruction. The apparent fractionation incorporates a number of different fractionation steps, namely the biosynthetic fractionation (which may be more or less constant for a given lipid, based on the current literature) and the evapotranspirative enrichment in soil and leaf water. Hence, a modern apparent fractionation represents the current balance between these fractionations, i.e. represents the current hydrological state of the catchment ecosystem. In that sense, the observed offsets in apparent fractionation between plant functional types may be due to a) differences in evapotranspirative enrichment and/or b) biosynthetic fractionation (see Sachse et al., 2012). But in the paleorecord, especially during major climatic changes, the evapotranspirative enrichment will likely change and either amplify (drier) or diminish (wetter) the leaf wax δD signal. Additionally, vegetation changes (such as grasses vs trees) may affect the overall biosynthetic fractionation. Suggesting a constant apparent fractionation to be applied for paleoenvironmental reconstruction of say $96 \pm 8\%$ implies that it will be possible to reconstruct source water δD values from leaf wax δD values with an error of $\pm 8\%$. Based on what I outlined above, I don't think that's possible, as long as no additional data exist to estimate past changes in evapotranspirative enrichment and vegetation cover.

Minor Issues:

p 3720, l19: Not all hydrogen in all organic matter derives from meteoric water, algae would use lake water or ocean water and heterotrophic organisms may use organic substrates as H sources

p3720, l25: This sentence sounds like only the continental effect is reflected in leaf wax δD , but all factors affecting precipitation δD are ultimately integrated into the δD_{wax}

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signal.

p3721, l2: in Sachse et al 2006 we did not present any data from the geological record, so citation doesn't fit here.

p3721, l7: relative humidity affects soil and leaf water evapotranspiration so no need to mention it here as a complicating factor on δD_{wax} . What is meant with water use here specifically? The Craig & Gordon 1965 citation doesn't fit here, as they did not investigate δD_{wax} .

p3721, l13: in Sachse et al. 2006 we did not investigate n-alkanoic acids, so citation doesn't fit here.

p3721, l15: Short-chain fatty acids <22 carbon atoms are present in almost every living organism, also in higher plants, so no, they are not generally used as aquatic biomarkers.

p3722: see comment 1), the cited studies investigated n-alkanes, with the exception of Hou et al 2007

p3722,l14: Which isotopic fractionation, net? biosynthetic?

p3722,l24: What is meant with 'correlations with climate' here?

p3725: Equation 1 should be written according to the current nomenclature, i.e. without the factor 1000 which is implied by reporting delta values in permil, see (Coplen, 2011)

p3727, l5: Which FAMES were measured as a performance test? I ask, because I would avoid using an n-C15 alkane as an internal standard, because of its volatility (and less so a n-C14 alkane). Under certain conditions (i.e. aged liner), especially when the GC temperature program starts with a relatively high value of 80°C, fractionation could occur in the injector and may introduce a bias into the correction. We find, when starting at 60 or 70°C that values of n-alkanes from a standard mixture with less than 16 carbon atoms are often associated with larger standard deviations and larger

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offsets to their real values as heavier n-alkanes. Additionally, a C38 alkane has a very high boiling point and it can be difficult to get a well defined peak for these heavy compounds, as they elute during the isothermal phase of the GC temperature program. Essentially, standards should be as similar to the target compounds as possible, so using the FAME mix for normalization with presumably similar carbon number range as the target compounds, would be more reliable and less prone to the issues described above.

p3731, l9: There seems to be a typo it should be -24.23‰ instead of 24.23‰. I assume.

p3732, l2: Ficken et al 2000 actually show that there are substantial amounts of C20 and C22 n-alkanoic acids present in terrestrial plants.

p3780,l2: The net fractionation value of -94‰ \pm 21‰ from Feakins & Sessions 2012 was derived from n-alkanes, the absolute number is therefore not comparable with the values derived here for n-alkanoic acids (see comment 1).

Tables & Data:

Table 1: Please report standard deviations for water isotope measurements

Table 2: Please report standard deviations of n-alkanoic acid dD values. Also, if the precision of the instrument is not below 1, no significant digits should be reported, i.e. round values.

Figures:

The manuscript contains a lot of figures, some are not really essential (2, 6 and 10).

Fig 2 is nice, but doesn't convey an essential message needed for the paper, I suggest to delete it.

Fig. 5: Is this rain and snow together? Could these be plotted in different colors or symbols?

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Fig. 6: Not really needed, can be presented in a table and mentioned in the text.

Fig 10. Fig not needed, such a scheme is found in any textbook about isotope hydrology.

Fig 11: there is no legend explaining the color codings of the bars.

References:

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Coplen, T. B. (2011). Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. *Rapid Communications in Mass Spectrometry*, 25(17), 2538–2560. doi:10.1002/rcm.5129

Hou, J., D'Andrea, W. J., MacDonald, D., & Huang, Y. (2007). Hydrogen isotopic variability in leaf waxes among terrestrial and aquatic plants around Blood Pond, Massachusetts (USA). *Organic Geochemistry*, 38(6), 977–984. doi:10.1016/j.orggeochem.2006.12.009

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Jetter, R., & Schäffer, S. (2001). Chemical composition of the *Prunus laurocerasus* leaf surface. Dynamic changes of the epicuticular wax film during leaf development. *PLANT PHYSIOLOGY*, 126(4), 1725–1737.

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