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Discussions

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

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Dear Editor,

Thank you for the careful and thoughtful comments provided by the two reviewers. We really appreciate their insightful and constructive comments and feel corrections based on them have improved the quality of the revised manuscript.

RC1 (First reviewer’s comment) 1) Page 3720 line 10 Text should specify which leaf wax compound throughout. Later text suggests this refers to C30 n-alkanoic acid/precipitation, but as several different fractionations are discussed (alkanes, alkanoic acids, stream water, precipitation) the meaning of Dwax and epsilon should be

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specified throughout for clarity.

AC (Author's comment) Indeed, several different fractionations are presented and discussed throughout the paper. In particular, we define δDwax as a mass-weighted mean δD n-alkanoic acid value calculated to provide a common basis for comparison of the δD of different species regardless of chain length abundances (Page3732, lines 13-14). Clarifications as to which are being discussed have been added here (e.g.)"…between source water (precipitation) and nC30 leaf wax lipids (e.g. εC30/precip mean value is -105± 13‰ …" and throughout the manuscript where applicable.

RC1 (First reviewer's comment) 2) Page 3720 line 12: The authors infer that the leaf wax proxy is recording close to an average annual precipitation isotopic composition, although also suggest a possible bias is towards winter precipitation. The reasoning could be elucidated further in the text of the discussion. Does this imply a mechanism related to water availability (in an arid Arctic context), rather than a bias towards the growing season of the plants suggested elsewhere (Feakins et al., 2012; Sachse et al., 2009)?

AC (Author's comment) As suggested by the reviewer, we expanded on our reasoning for a possible winter bias in the δD leaf wax proxy and added the following paragraph in the discussion (Section 5.2.1): "The climate signal preserved in alkanoic acids from modern vegetation within the El'gygytgyn Basin closely reflect the isotopic composition of mean annual precipitation, with a possible bias towards winter precipitation due to the nature of water availability in an arid Arctic context. Within arid Arctic regions, and particularly at this site, snowmelt is the dominant annual hydrological feature (Nolan and Brigham-Grette 2007; Nolan, this issue; see section 5.1, pages 3735-3736). Given the presence and depth of extensive permafrost within the basin, this precludes deeper groundwater input and the majority of water available for plant uptake occurs as rapid drainage of snowmelt (i.e. winter precipitation) through the shallow active layer. The short growing season in this region -coinciding with warmer temperatures and enhanced snowmelt- also contributes to growth and production of biomass utilizing soil moisture dominated by stream water (active layer runoff) carrying a large winter precipitation signal offset by some input of isotopically enriched summer precipitation. Soil moisture data in this basin also shows individual summer precipitation events have only a minor effect on soil moisture content (Federov et al., this issue). Thus, water availability may be the primary mechanism by which the isotopic composition of mean annual precipitation is recorded by the leaf wax proxy in the El'gygytgyn Basin."

RC1 (First reviewer's comment) 3) Page 3722, line 4-13. The discussion mixes values for alkanes and alkanoic acids which may have offsets (Chikaraishi and Naraoka, 2007), so the text should maintain the compound specific origins, so as not to oversimplify.

AC (Author's comment) The following sentences have been added to clarify meaning within this paragraph:" Net fractionation values incorporate soil-water evaporation, leaf-water transpiration and biosynthetic fractionations (see Sachse et al., 2012 for review and references therein). Prior studies have shown smaller εl/w values for lake sediments from arid regions (n-alkanoic acids: Hou et al., 2008; n-alkanes: Polissar and Freeman, 2010) and for modern vegetation in drier vs. wetter sites (Smith and Freeman, 2006; Feakins and Sessions, 2010). "

RC1 (First reviewer's comment) 4) Page 3722, Line 18 For life form discussion of plant life forms please reference expanded dataset analyzed in (Sachse et al., 2012).

AC (Author's comment) Reference to Sachse et al. (2012) and expanded dataset therein included.

RC1 (First reviewer's comment) 5) Page 3724, section 3.1.2 This is an intriguing use of herbarium samples – primarily for botanical and pollen studies – also being used for leaf wax studies. There has only been one prior such study Yang et al., (2011). As this is an approach that could more widely be used from existing and new herbarium specimens, it would be nice to see a few more details on the sampling approaches published in the leaf wax literature: how much leaf tissue is collected for herbarium specimens, how are they fixed onto paper, at what stage were leaf tissues for wax studies removed, how much material was removed for the leaf wax isotopic studies, any particular sampling considerations and protocols?

AC (Author's comment) Additional information on treatment of herbarium samples used in this study is now provided in the methods section (Section 3.1.2 - Modern vegetation samples).

RC1 (First reviewer's comment) 6) Page 3732, line 1 It is known that C20-C32 n-alkanoic acids are made by terrestrial plants (n=3) emergent plants (n=3) and submerged and floating plants (n=3) (Figure 1; Ficken et al., 2000). Part of the confusion has arisen because this early study has been mis-represented as showing mid chain leaf wax compounds are made by aquatic plants, whereas in fact it is only in mid chain n-alkanes that a distinction was observed. That study found mid chain n-alkanoic acids at in similar relative abundances in terrestrial plants (n=3), emergent plants (n=3) and submerged and floating plants (n=3) (Figure 1; Ficken et al., 2000). The finding of mid chain n-alkanoic acids in terrestrial plants is also corroborated here. The corresponding introduction should therefore not imply that mid chain alkanoic acids are markers for aquatic plants.

AC (Author's comment) We agree that the data presented in Ficken (2000) does show the production of C20-C24 n-alkanoic acids by terrestrial (n=3) and emergent plants (n=9) as well as by submerged/floating macrophytes (n=8). Indeed, our data directly supports significant production of C20-C24 acids by terrestrial vegetation (Table 2). However, Figure 1 of Ficken et al. (2000) does depict clear differences in the relative percent of C20 and C22 alkanoic acids in submerged/floating macrophytes vs. emergent or terrestrial plant types with greater percentages of C20 and C22 acids found in submerged/floating plants. Further, Ficken et al (2000) state: "…when all three classes of lipid are considered (Fig. 1), the n-alkanes exhibited the most significant differences in distribution between the three plant types." …which does not preclude observable

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differences in distributions in the remaining compound classes albeit less pronounced.

7) Page 3743, line 27 "Differences between samples are more likely due to randomly distributed net fractionations rather than a systematic offset between woody vs. grass samples (as predicted for high latitudes)." The meaning of this sentence is unclear, particularly the section in parentheses. An earlier statement said that there was no evidence for life form offsets in this survey, given that only 7 species are sampled perhaps this is inconclusive?

AC (Author's comment) We agree that given the small data set presented here this is likely inconclusive and the text has been modified accordingly and text in parentheses removed.

8) Page 3744, line 6 It is not clear why the sedimentary fractionation emphasized for paleoclimate work at the end of the conclusion is not also represented in the abstract; there the modern plant value is instead highlighted.

AC (Author's comment) We added the following sentence to the abstract: "A net fractionation calculated for 200 yr-integrated lake sediments yields ε30/precip = -96 ±8‰ and can provide a basis for application of this proxy downcore. "

RC1 (First reviewer's comment) Technical corrections: 9) Page 3727, line 3 Report the _D values of the C15 and C38 n-alkanes used for normalization to the 2-point VSMOW-SLAP isotopic scale (Coplen, 2011). AC (Author's comment) Included values for all isotopic standards used in this study (obtained from A. Schimmelmann, Indiana University) where indicated.

10) Page 3733, line 15 Remove the definition of ACL, repeated from above. AC (Author's comment) Duplicate description deleted.

11) Page 3738 The text could be rephrased to improve clarity on lines 7-21. Line 7 suggest to remove 'yet, despite: : : lake sediments'. Line 10: 'these 7 sampled species: : : we calculated an unweighted average (Fig. 11). This unweighted average was then: :

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:'. Line 18 'The average appears particularly sensitive to Bryophyta weighting.' AC (Author's comment) As suggested by the reviewer, we rephrased the sentences on lines 7-21: In order to evaluate how representative the 7 sampled species are of all vegetation within the basin, we calculated an unweighted average distribution of compounds (Figure 11). This unweighted average was then used to produce a representative assemblage of n-alkanoic acids within the El'gygytgyn Basin (Figure 11).

12) Page 3744, line 6 Recommend reporting the _D value to 0 decimal places throughout (consistency and appropriate precision). AC (Author's comment) Values reported have been modified accordingly, in text and within tables and figures.

13) Table 2 Epsilon terms need clearer definition within the table (e.g., which chain length). Column 1 sample names are hard to read as formatted. Appropriate to report to 0 decimal places. AC (Author's comment) Font size increased and column width adjusted for sample names in Table 2. Definitions added for epsilon terms and for δDwax. Reported values modified accordingly.

14) Figure 8 Specify the chain length of 'wax'? AC (Author's comment) δDwax was changed to δD30 acid to clearly define chain length and values reported in Figure 8.

15) Figure 11 Figure 7 and 8 have a color coded caption, but chain length information is missing from Figure 11. AC (Author's comment) Colour coded legend added to Figure 11.

âĂČ RC2 (Second reviewer's comments) 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 at 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‰ _ 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 of the study more clearly. But this also requires to put the current data in perspective with previously published alkane as well as alkanoic acid data, as the absolute values cannot be directly compared between n-alkanes and n-alkanoic acids.

AC (Author's comment) As previously suggested by Reviewer 1, greater clarification between the compound classes (n-alkane vs n-alkanoic acid literature) has been attempted throughout the revised text.

Novel viewpoint: We appreciate reviewer's 2 comment here and have also attempted to highlight this study's contribution to the currently limited data for controls on the δD values for alkanoic acids for paleoclimate reconstructions.

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 (dryer) or diminish (wetter) the leaf wax dD 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_8‰ implies that it will be possible to reconstruct source water dD values from leaf wax dD values with an error of _8‰ËŹ ased 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.

AC (Author's comment) We agree that the modern apparent fractionation presented here represents the cumulative current balance between multiple fractionations and specifically the hydrological state of the catchment. However, although not the focus of this manuscript, application of modern apparent fractionation in paleoenvironmental reconstruction may be possible within this basin as part of a multi-proxy synthesis. Additional paleoenvironmental data and independent proxy reconstructions are available and ongoing for this site: data on past changes in vegetation cover is available through detailed palynological studies; independent investigation of the lake water isotopic composition through analysis of δ18Odiatoms (Chapligin et al., 2012; this issue); and hydrological change and lake level variations (Federov et al., this issue).

Minor Issues: p 3720, l19: Not all hydrogen in all organic matter derives from meteoric water, algea would use lake water or ocean water and heterotrophic organisms may use organic substrates as H sources AC (Author's comment) As we point out in later paragraphs (pg 3721) and in Fig. 10, there are certainly distinct pools of environmental waters which different organisms utilize, recording different environmental effects. However, we have clarified the sentence here: "Environmental water is the primary source of hydrogen for organic matter from photoautotrophic organisms; for terrestrial plants, this constitutes soil water that is ultimately driven by precipitation (see Sachse et al., 2012 for review). Multiple environmental variables affect the δD values of meteoric water such as temperature, elevation and water vapour source (Craig, 1961;

Dansgaard, 1964; Gonfiantini, 1986; Gat, 1996). “

p3720, l25: This sentence sounds like only the continental effect is reflected in leaf wax dD, but all factors affecting precipitation dD are ultimately integrated into the dDwax signal. AC (Author’s comment) We hope this is clarified in combination with the above revised text (preceeding sentence) as both sentences refer to factors affecting the δD values of meteoric water.

p3721, l2: in Sachse et al 2006 we did not present any data from the geological record, so citation doesn‘t fit here. AC (Author’s comment) Reference has been corrected to Sachse et al. 2004 and text changed to refer to ”...sedimentary δDwax...” to distinguish lipids found in sediments rather than modern/ living vegetation.

p3721, l7: relative humidity affects soil and leaf water evapotranspiration so no need to mention it here as a complicating factor on dDwax. What is meant with water use here specifically? The Craig & Gordon 1965 citation doesn‘t fit here, as they did not investigate dDwax. AC (Author’s comment) Reference removed. Water use was in reference to physiological differences relating to plant life form, specifically in reference to difference n rooting depth and usage of potentially different soil waters with depth. This is a minimal factor at Lake El’gygytgyn given the shallow active layer and rapid drainage limiting soil water residence times and possible soil water enrichment due to evaporation/ aridity.

p3721, l13: in Sachse et al. 2006 we did not investigate n-alkanoic acids, so citation doesn‘t fit here. AC (Author’s comment) Reference removed.

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. AC (Author’s comment) Text changed to indicate short chain fatty acids of <20 carbon atoms and their overall greater relative abundances from phytoplanktonic and zooplanktonic sources (i.e. Volkman et al., 1998).

p3722: see comment 1), the cited studies investigated n-alkanes, with the exception of Hou et al 2007 AC (Author’s comment) Paragraph has been rewritten to clarify sources. (e.g. “. . .Prior studies have shown smaller εlipid/w values for lake sediments from arid regions (n-alkanoic acids: Hou et al., 2008; n-alkanes: Polissar and Freeman, 2010) and for modern vegetation in drier vs. wetter sites (n-alkanes: Smith and Freeman, 2006; Feakins and Sessions, 2010). . . .”) In particular, we indicate fractionations with the subscript “lipid” to be inclusive of both compound classes as they show similar trends, despite the small data set for alkanoic acids.

p3722,l14: Which isotopic fractionation, net? biosynthetic? AC (Author’s comment) Text modified: “. . .In addition to variable climatic and/or biosynthetic drivers affecting net fractionations, large interspecies variability has been found at the individual plant scale. . .”

p3722,l24: What is meant with ‚correlations with climate‘ here? AC (Author’s comment) Our intent was to highlight the strong correlation between ïĄd’D of source water and average ïĄd’Dwax values from leaf wax lipids in sediments due to temporal and spatial integration of plant inputs. Although the reduced variability in these data sets (vrs individual organisms) may not capture the full range of values observed in modern environments, the ‘smoothing’ inherent with integration may better reflect climate trends (i.e. proxies may truly represent ‘climate’ signal rather than ‘weather’). Text slightly modified: “. . .better correlations to climate than studies of individual plants due to temporal and spatial integration of plant inputs.”

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) AC (Author’s comment) This has been corrected.

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 it‘s volatility (and less so a n-C14 alkane). Under certain conditions (i.e. aged liner), especially

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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 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. AC (Author's comment) FAME standard mixture consisted of C16:0, 18:0, 20, 22, and C30 FAMEs, targeting our compound range of interest. These were run daily with the n-alkane isotopic standards with good reproducibility. We did observe greater variability in the nC14 alkane, however this compound was never used for correction. The n-C38 peak was broad due to its elution during the isothermal phase, however for the majority of samples there were no co-elution problems and good baseline separation was achieved (with only minor exceptions). With respect to your comments regarding use of the FAME mix for normalization, we reviewed the raw data and reevaluated using the FAME mixture for normalization. The reevaluated data yielded similar values within error from the original normalization using the co-injected n-alkane isotopic standards.

p3731, l9: There seems to be a typo it should be -24.23‰ instead of 24.23‰ I assume. AC (Author's comment) Typo corrected.

p3732, l2: Ficken et al 2000 actually show that there are substantial amounts of C20 and C22 n-alkanoic acids present in terrestrial plants. AC (Author's comment) Please see AC for Reviewer 1, comment 6. Notably: Figure 1 of Ficken et al. (2000) does depict clear differences in the relative percent of C20 and C22 alkanoic acids in submerged/floating macrophytes vs. emergent or terrestrial plant types with greater percentages of C20 and C22 acids found in submerged/floating plants. We do not dispute the presence nor production of these compounds in terrestrial plants (our data also show this) but the relative abundances of these compounds are shown to be greater in submerged/floating macrophytes.

p3780,l2: The net fractionation value of -94‰ +/-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). AC (Author's comment) Text has been revised to clarify compound sources used to calculate fractionation values and direct comparison of values avoided. "…Net fractionation between long chain (C27, C29 and C31) n-alkanes and source water in arid to semi-arid ecosystems also display similar values (-94 ± 21‰ $FeakinsandSessions, 2010)althoughn -$ $alkanoicacidsareexpectedtobeenrichedinDcomparedton -$ $alkanesfromthesamesourcebyabout25\pm$ 16‰ based on their biosynthetic origins (Chikaraishi and Naraoka, 2007). …"

Tables & Data: Table 1: Please report standard deviations for water isotope measurements AC (Author's comment) Done.

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. AC (Author's comment) Values reported have been modified accordingly, in text and within tables and figures.

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. AC (Author's comment) Figures 6 and 10 have been removed and data from Fig 6 now presented in Table 3. We retain Figure 2 for best possible spatial representation of δD stream data, surrounding topography and locations of sediment trap sampling within the basin.

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

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symbols? AC (Author's comment) Figure 5 has been adjusted so rain and snow are now plotted with different colours.

Fig. 6: Not really needed, can be presented in a table and mentioned in the text. AC (Author's comment) Figure 6 has been removed and data now presented in Table 3.

Fig 10. Fig not needed, such a scheme is found in any textbook about isotope hydrology. AC (Author's comment) Figure 10 removed.

Fig 11: there is no legend explaining the color codings of the bars. AC (Author's comment) Colour coded legend added to Figure 11.

Interactive comment on Clim. Past Discuss., 8, 3719, 2012.