

Responses to comments from Reviewer#2:

**We appreciate the comments from Reviewer #2.**

I have read the manuscript several times but found it hard to follow as it was poorly organized. General speaking I don't think this manuscript merits publication in Biogeosciences. Many conclusions seemed arbitrary and overstated.

The authors apparently neglected the species effect. The manuscript was targeted to address the effect of environmental factors on leaf wax *n*-alkane distributions and hydrogen isotopes. However, only species, *Sphagnum* was specified, while all the rest of higher plants were mystery to readers. The sites of peat bogs chosen covered latitudinal shift from 25 to 42\_N, i.e. a very big latitude range. The types of higher plants, say, C3/C4 plants, gymnosperms/angiosperms, etc are expected to vary significantly from south to north, and so were the distributions of *n*-alkanes. Surprisingly, the authors did not analyze any samples of leaf waxes from "leaves" but arbitrarily attributed the differences in CPI and ACL among different peat bogs to pH, conductivity, etc. The input ratios from different plants (including *Sphagnum*) actually determined the ACL and CPI. For example, the alkane distribution in Fig. 2A (Zoige) was characterized by two centers, suggesting at least very different types of input. A calculation of ACL in Zoige peat bog based on such distribution and then relating it to pH, ORP etc is actually misleading. The authors simply piled a bunch of R2 in Tables 2-5 without giving data of *n*-alkane distributions. Are there coexistences of alkenes indicating aquatic sources? The authors ought to characterize and quantify *n*-alkane from different sources before any link to environmental factors.

**Reply: Peatlands are a depositional setting quite different from others, such as lakes or soils; in-situ plants predominate the organic sources in peat deposits (Farrimond and Flanagan, 1996; Pancost et al., 2002). The waterlogged conditions prevailing in peatlands do not favor the growth of C4 plants. In addition, all the surface peat samples collected in this study were from moss and herb dominated sites. Thus differences in plant types of higher plants, such as C3/C4 plants, gymnosperms/angiosperms, could be not the major factors controlling the alkane ratios and dD ratios of the leaf wax *n*-alkanes in these peat samples.**

**Although these samples were retrieved under *Sphagnum* lawns, the distribution patterns of long chain *n*-alkanes suggest that peat mosses are not their main sources. The reasons probably result from the preferential degradation of medium chain *n*-alkanes or the low yield of *n*-alkanes in mosses relative to vascular plants (Pancost et al., 2002; Huang et al., 2014). The concentration of long chain *n*-alkanes is normally one magnitude lower in fresh peat mosses than those in fresh vascular plants.**

**In summary, we argue that vascular herbaceous plants are the dominant sources for the long chain *n*-alkanes in this study and that environmental factors such as temperature and precipitation are the important controllers on their distribution patterns in peatlands.**

Fig.2 also showed large amplitudes of dD values of a single compound within one given peat bog. Such phenomenon can be attributed to the fact that distributions of alkanes in a peat bog were indeed

NOT homogeneous, which are distinct from lake sediments. Except the Shiwangutian, the amplitudes of dD values of a single compound in the other 3 peat bogs are so big that the differences in this manuscript could be simply due to sampling strategy.

**Reply: We do not agree with the comment that the amplitudes of dD values of a single site are due to sampling strategy. This phenomenon may be a common feature, at least in peatlands. Eley and colleagues (2014) reported similar patterns in a UK saltmarsh. Such a heterogeneity may result from the dD of soil waters depending on micro-environments. Certainly the heterogeneity of n-alkane dD ratios in a single peatland merits caution when the alkane dD ratios have a relatively small amplitude. For large spatial gradients, equaling larger temporal scales, both temperature and precipitation have larger amplitudes and thus could be the primary controllers on peat alkane dD ratios. In this case, it would be better to collect adequate samples and compare the averaged means among different peatlands, to eliminate the variations in micro-habits.**

Authors listed six sites of peat bogs for this study but only presented some of them. Such selection seemed arbitrary as authors simply wanted to present “good correlations”. In addition, even with such arbitrary selection, almost all correlations between pH, conductivity or ORP with dD of long chain n-alkanes were actually poor, with almost all  $R^2 < 0.5$ . However, the authors consider them as strong correlations. For that size of samples and such weak  $R^2$ , I feel that the conclusions were too overreached. The authors did not provide any explanation how pH, ORP or conductivity affects ACL or dD values of a single compound. What is the mechanism? For example, can microbial activity significantly modify the CPI/ACL and reduce C23 and C25 abundances in the peat samples, and how was such activity affected by pH, ORP? The manuscript did not provide any insight for the community, but more like a bunch of data piled up and listed weak correlation with so-called environmental factors.

Currently the authors took for granted that distributions of n-alkane input to each bog were the same but ONLY those environmental factors changed their composition so that they considered the  $R^2$  between pH, conductivity or ORP and ACL/CPI. That is certainly not the case. The environmental factors such as temperature, precipitation actually controlled vegetation type and affected distribution of alkanes. Furthermore, the formation of peat bog is a process of long time. However, the data of temperature and precipitation given in this paper (for example, Fig. 3) were from a given year.

**Reply: The number of peatlands in this study is seven not six. Peatlands except Zoige have similar plant communities dominated by *Sphagnum*, acidic pH and relatively low conductivity, while the Zoige has basic pH and quite high conductivity and no peat moss. Thus it is not arbitrary to remove Zoige from the peatland batch.**

**We admit that it is not wise to calculate the correlation between alkane ratios/dD ratios and water chemistry. The alkane ratios and dD ratios integrate information from a relatively long period, perhaps several years to decades to accumulate 2 cm peat. In contrast, the water chemistry is only a single measurement of today’s condition. These chemical parameters surely have daily and seasonal variations. The annual air temperature and precipitation, however, are**

**long term averaged values and parallel the alkane ratios. We will delete the discussion on the relations between alkane ratios and water chemistry in the revised text.**

In the last sentence of the Abstract “the dDalk ratios of n-C29 and n-C31 alkanes as sensitive paleohydrologic proxies on millennial and larger timescales.” How do authors know such proxies can be applied in such larger time scales?

**Reply: This sentences was rephrased as “environmental factors such as temperature and precipitation are the primary controllers on the dDalk ratios of n-C29 and n-C31 alkanes in peat deposits”.**

I also have a big concern on the calculation of dalk/p. In the Method the authors stated  $\delta A_c d' DP$  was estimated from an online calculator. It is generally OK, but for those peat bogs located at altitudes from 900 to 1700 m asl, Rayleigh fractionation could cause large fraction in precipitation. The samples were collected in a two year period. Did authors think about the change in the amount of precipitation during the two year period? Amount effect would lead to the variations of precipitation dD values.

**Reply: The estimated dD with the online calculator has considered the elevation from each site. In addition, the estimated dD values do not specifically constrain to which year; it is an annual averaged value.**

In summary, there are too many arbitrary statements and they are simply not convincing to me.

Specific comments: 1) Equation (1) was completely wrong. It is a fundamental concept and should have not been wrong!

**Reply: We are sorry for such a spelling mistake. We indeed utilized the right equation during data calculation.**

2) There are quite a bit colloquial expressions. For example, Page 15163, Line 4, “Either way, the new and previous results suggest caution”

**Reply: We have checked the text and changed these expressions.**

## **References**

1. Eley, Y., Dawson, L., Black, S., Andrews, J., Pedentchouk, N.: Understanding  $^2H/^1H$  systematics of leaf wax *n*-alkanes in coastal plants at Stiffkey saltmarsh, Norfolk, UK, *Geochim. Cosmochim. Acta*, 128, 13-28, 2014.
2. Pancost, R. D., Baas, M., van Geel, B., Sinninghe Damsté, J. S.: Biomarkers as proxies for plant inputs to peats: an example from a sub-boreal ombrotrophic bog, *Org. Geochem*, 33, 675-690, 2002.
3. Huang X., Xue J., Wang X., Meyers P.A., Gong L., Liu Q., Qin Y., Wang H. Hydrologic influence on  $\delta^{13}C$  variations in long-chain *n*-alkanes in the Dajihu peatland, central China. *Org. Geochem.*, 69, 114-119, 2014.

4. Farrimond P., Flanagan R. L., Lipid stratigraphy of a Flandrian peat bed Northumberland, UK: comparison with the pollen record. *Holocene* 6, 69-74, 2014.