Reply to Referee#2 Marie Galeron

We thank Marie Galeron for her constructive and detailed comments and suggestions on our manuscript. In the following we address all issues raised in her review.

Referee#2: My main concern with this manuscript is the small number of samples used to build the conceptual model. While I understand that the model can be drafted with such few samples, it should be made clear in the manuscript that the conceptual model is not a tool ready for a research use at this stage. The bias observed between the model outputs and the actual modern RH values/ ^2H leaf enrichment could be a concern since the model is not solidly built on a large number of observations.

Response: Please note that the coupled $\delta^2H_{n\text{-alkane}}$-$\delta^{18}O_{sugar}$ model is not based on the 20 samples analysed in this study for $\delta^2H_{n\text{-alkanes}}$ as assumed by both Reviewer#1 and Marie Galeron. Indeed this is a conceptual model (see title of the respective subchapter 2.4) and for further details on the model we refer our readers to Zech et al. 2013 at the end of the chapter. The 20 samples from the presented Argentinean climate transect are rather used for validating the conceptual coupled $\delta^2H_{n\text{-alkane}}$-$\delta^{18}O_{sugar}$ model.
→ In order to make this more clear, we (i) slightly changed the title and included amongst others " – a climate transect validation study", (ii) restructured and reformulated the abstract, (iii) reformulated the aims of our study at the end of the introduction chapter and (iv) slightly rewrote the conclusion chapter.

Referee#2: Another concern is the assumption that the studied n-alkanes and hemicellulose markers are leaf-derived. I agree that these compounds tend to be tracers of terrestrial higher plants, and more precisely leaves, but there is very little description of the actual vegetation found in sample sites along the transect. There seems to be quite a variation in climate and vegetation across sites, and while I can agree that in the tropical humid areas, leaves will rapidly feed the topsoil layer sampled, without further description, the more arid areas, with hardly any leafy vegetation, could have a different profile. Please provide details on species/types of vegetation encountered at sampling sites.

Response: Following the recommendation of Marie Galeron, we included the dominant plant genus in the Material and Method section. Furthermore, we refer our readers to Tuthorn et al. (2014) and now additionally also to Ruppenthal et al. (2015), where maps illustrate the distribution of vegetation zones in the study area and to several references focussing on vegetational research in Argentina. Concerning the leaf-origin of the investigated biomarkers, we agree with Marie Galeron that this is one of the major uncertainties for our conceptual coupled $\delta^2H_{n\text{-alkane}}$-$\delta^{18}O_{sugar}$ model. We therefore openly discuss the option of stem, root and soil microbial contributions in our MS and complemented the discussion during revision by including that "..there is strong evidence suggesting that *n*-alkanes are not significantly introduced into soils/subsoils by roots (Häggi et al., 2014)."

Referee#2: The source of fatty acids could be numerous (discussed on p. 2468, lines 18-23) – maybe some sampling locations deserve an estimation of leaf-derived vs. non -leaf derived material?

Response: While we agree with Marie Galeron that a quantitative estimation of leaf-derived versus non-leaf-derived fatty acids would be desirable, we consider this aim to be very ambitions and hardly possible based on the available data.

Referee#2: The Global Meteoric Water Line (concept and uses) should be defined in the manuscript.

Response: Included and rewritten at the beginning of chapter 2.4. Conceptual model for a coupled $\delta^{18}O$-$\delta^{2}H$ biomarker approach

Referee#2: "Based on the premise that n-alkanes and hemicellulose biomarkers are primarily leaf-derived, we reconstruct $\delta^{2}H$leaf water and $\delta^{18}O$leaf water, respectively, which in turn allows assessment of the d excess of leaf water. The large calculated range in d excess along the transect (-67 to -178 ‰) can be used to calculate/model RH;"
The leaf water reconstructions, in turn, feed the RH reconstruction model. But RH is needed to estimate transpiration rates used in the leaf water reconstruction model? Isn't that an issue when coupling the models?

Response: Please allow us to clarify that two models were used in our study.
First, (chapter 2.3. and 3.2.) we used a Péclet-modified Craig Gordon model (Kahmen et al., 2011) in order to (i) estimate leaf water enrichment, (ii) support the notion that RH is the main controlling climatic factor and (iii) *n*-alkanes and fatty acids of the topsoils reflect the isotopic composition of precipitation modified by leaf water enrichment.
Second, the conceptual coupled $\delta^{2}H_{n\text{-alkane}}$-$\delta^{18}O_{sugar}$ model (chapter 2.4. and 3.3.). Here, we reconstruct biomarker-based $\delta^{2}H/\delta^{18}O_{leaf\ water}$ values by correcting for biosynthetic fractionation factors. The reconstructed biomarker-based $\delta^{2}H/\delta^{18}O_{leaf\ water}$ values are then used for calculating RH values.

Referee#2: P. 2472, lines 13-28. This paragraph is confusing, Line 25 "However, give that this…": what does "this" refer to?

Response: Paragraph rewritten and simplified (partly deleted)

Referee#2: Figure 3: The caption/legend could be clearer.

Response: Following the recommendation of Marie Galeron we added: "Comparison of measured $\delta^{2}H_{n\text{-alkanes}}$ (weighted mean of n-C_{29} and n-C_{31}) and $\delta^{2}H_{fatty\ acids}$ (weighted mean of n-C_{22}, n-C_{24}, n-C_{26}, n-C_{28} and n-C_{30}) pattern with $\delta^{2}H_{prec}$ (Bowen, 2012) along the north-south climate transect (^{x}min and $^{+}$max representing annual minimum and maximum value at the sampling site)."

Referee#2: Figure 5: May be too complicated. Evaporation Lines and GMWL needs to be clearly defined in the text. The legend is not clear as to what it is exactly that is reprensented. What is the main message that this figure should convey?

Response: In order to make the message of this figure clearer, we rewrote the caption. It now reads: "Fig. 5: $\delta^{18}O$-$\delta^{2}H$ diagram illustrating the conceptual model of the coupled $\delta^{2}H_{n\text{-alkane}}$-$\delta^{18}O_{sugar}$ approach (modified after Zech M. et al., 2013a). $\delta^{2}H_{n\text{-alkane}}$ (mean of n-C_{29} and n-C_{31}) and $\delta^{18}O_{sugar}$ (mean of arabinose, fucose and xylose) results are used to reconstruct $\delta^{2}H/\delta^{18}O_{leaf\ water}$ by subtracting the biosynthetic fractionation factors. The deuterium excess ($d = \delta^{2}H - 8 \times \delta^{18}O$) of leaf water serves as proxy for RH and $\delta^{2}H/\delta^{18}O_{prec}$ is calculated as intersection of the individual evaporation lines (ELs, slope 2.82) with the global meteoric water line (GMWL)."
Furthermore, we changed the symbols (both in the graph and the legend) and rewrote chapter 2.4. Conceptual model for a coupled $\delta^{2}H$-$\delta^{18}O$ biomarker approach.

Referee#2: Figure 7: Is this figure necessary?

Response: Yes, it illustrates one of the main results of our MS, namely the highly significant correlation of modern 'actual' $\delta^2H/\delta^{18}O_{prec}$ with biomarker-based 'reconstructed' $\delta^2H/\delta^{18}O_{prec}$.

Referee#2: There are a number of issues with the reference list:

- *Should the last Zech et al. reference in the list (2013) be 2013c? Please update in the manuscript as well.*
- *Huang, Y., Shuman, B., Wang, Y., and Webb, T.: Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test, J. Paleolimnol., 31, 363–375, 2004. : not cited in the text*
- *Cited in the text but missing from the reference list :*
  - *Gessler et al., 2009 (P. 2472, line 25)*
  - *Kahmen et al., 2009 (P ; 2466, line 20)*
  - *Song et al., 2013 (P. 2466, line 20)*
- *In the manuscript, please remove b from Kahmen et al., 2011b reference (P. 2466, line 13, and P. 2472, line 3)*
- *P. 2464, line 17 : Zech et al., 2013 → a, b, or c ?*
- *P. 2472, line 3 : Tipple et al. → 2012 in the manuscript, 2013 in the reference list. Please fix date in the manuscript.*

Response: Thanks a lot for pointing us to these flaws → all corrected

Referee#2: Typos:

- *Please make sure the n in n-alkanes is in italics throughout the text*
- *P. 2462, line 26: "enrichment of leaf water being recorded in both, n-alkanes and…": please remove comma*
- *P. 2463, line 19: "sampling localities": should this be sampling locations?*
- *P. 2464, line 25-26: "The chromatograms of the other sampled…": should this read "The chromatograms of the other sampleS…"?*
- *P. 2465, line 20: space missing between "The" and "2H"*
- *P. 2469, line 28: please add comma after "enrichment of soil water", and replace "can possibly" by "could"*
- *P. 2472, line 1: "Third, given that leaf waxes considered to be…" : Should this read "Third, given that leaf waxes ARE considered to be…"?*

Response: Thanks a lot for pointing us to these flaws → all corrected