

Reply to A. Lücke (SC2: d-excess reconstruction)

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Hepp and co-workers present a very interesting and novel dual compound-specific isotope approach to paleoclimate reconstructions. Through combining the hydrogen isotopic compositions of long-chain n-alkanes with the oxygen isotope composition of arabinose they were able to determine d-excess values for the YD – Holocene transition at lake Gemündener Maar and, subsequently, infer relative humidity (RH).

→ We are very grateful to A. Lücke for his encouraging words and his constructive comments. Readily, we explain here in more detail why we consider our d-excess reconstruction to be robust and will include respective arguments in the revised manuscript where reasonable.

Their reconstructed leaf water d-excess values range between -125 and -30‰. Given the novelty of the approach and the importance of the reconstructed d-excess values for the following RH reconstruction an extensive discussion of the reliability of these values (irrespective of the analytical uncertainty) seems necessary and valuable. Is the wide range of reconstructed d-excess values for this site realistic, e.g. in view of modern leaf water d-excess?

→ Unfortunately, we are not aware of literature reporting on d-excess values of leaf water in or close-by to our study area. Still, our reconstructed d-excess values are realistic. For instance, Voelker et al. (2014) reported on ‘deuterium deviations’ (calculated as d-excess of leaf water minus 10‰). The deuterium deviation values in the respective publication (Voelker et al., 2014) range from ~0 to ~-200‰. Furthermore, Mayr (2002) conducted climate chamber experiments with *Vicia*, *Brassica* and *Eucalyptus* during his dissertation and measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of leaf water ($\delta^{18}\text{O}$ of leaf water and of stem sugar biomarkers are published in Zech et al., 2014). Accordingly, d-excess of leaf water ranged from -38 to -171‰ and correlated highly significantly with RH (ranging from 21 to 68%). The former hence confirms that the reconstructed d-excess values of the Gemündener Maar ranging from -30 to -125‰ are well within the range that can be expected; the latter nicely corroborates the coupled $\delta^2\text{H}_{n\text{-alkane}}\text{-}\delta^{18}\text{O}_{\text{sugar}}$ paleohygrometer approach that is applied in

our manuscript in order to reconstruct RH values. A respective manuscript is currently under revision.

How can the large “short term” variations of d-excess be explained?

→ That’s indeed a very interesting question. Concerning “short term”, it should be noted that the resolution of our Gemündener Maar record is on average 58 years according to our age-depth model. Moreover, the reconstructed d-excess of leaf water reflects RH changes. In our opinion, RH changes can have two main reasons. First, moisture supply from the Atlantic Ocean is and was variable depending on sea surface temperature and on atmospheric circulation patterns. Second, we pointed in our manuscript to the finding that centennial variability of RH history of Western and Central Europe seems to covary with solar activity and thus insolation (Fig. 6). Possibly, insolation minima reduced the warming up and thus drying of air masses on the continent. Given that the solar activity records based on ^{10}Be and ^{14}C shown in Fig. 6 also reveal pronounced decadal variability, we suggest that decadal RH variability in our record may have been triggered by insolation changes.

How would the reconstructed d-excess values change if the biosynthetic fractionation values used would be different or impacted by vegetation change and thus lead to different sedimentary long-chain n-alkane dD values? Larger changes of the terrestrial and lacustrine vegetation in the course of the Lateglacial – Holocene transition are well known. Species-specific effects seem likely not only between grasses and woody plants (as discussed regarding an overall signal dampening), but also between different woody plants (Hou et al., 2007). In addition, in a lacustrine environment the long-chain n-alkane composition (n-C27, n-C29) of sedimentary organic matter might be influenced by aquatic macrophytes (e.g. Aichner et al., 2010). Since the magnitude of fractionation between source water and biochemical compounds seems to be distinctively different for terrestrial and aquatic plants (Chikaraishi et al., 2004) even small amounts of macrophyte derived long-chain n-alkanes might have a considerable impact on the total sedimentary long-chain n-alkane dD value. A sensitivity study could potentially identify the degree of uncertainty introduced by respective relevant factors.

→ We fully agree with A. Lücke that the biosynthetic fractionation factor used to reconstruct $\delta^2\text{H}_{\text{leaf-water}}$ values from $\delta^2\text{H}_{n\text{-alkane}}$ results (and thus d-excess) is one of the major uncertainties of the coupled $\delta^2\text{H}_{n\text{-alkane}}-\delta^{18}\text{O}_{\text{sugar}}$ paleohygrometer approach. In order to provide the magnitude: a shift in the $\delta^2\text{H}_{n\text{-alkane}}$ biosynthetic fractionation of $\pm 10\text{‰}$ corresponds to a change in the reconstructed RH value of $\sim \pm 6\%$.

We acknowledge, that Hou et al. (2007) reported on significant variations in $\delta^2\text{H}_{n\text{-alkane}}$ within plant types. For instance, $\delta^2\text{H}$ of $n\text{-C}_{29}$ from trees ranged from -218 to -160‰ (mean = $-185\text{‰} \pm 13\text{‰}$). However, Hou et al. (2007) at the same time emphasized that the range of variation is clearly smaller than those among different plant types and that grasses have the lowest $\delta^2\text{H}$ values. $\delta^2\text{H}$ of $n\text{-C}_{29}$ in grasses ranged from -238 to -186‰ (mean = $-219\text{‰} \pm 18\text{‰}$). We therefore consider our calculations accounting for the dampening effect of leaf water enrichment (see Eqs. 10 and 11) as it occurs in grasses to be appropriate.

We are furthermore very grateful to A. Lücke for pointing to uncertainties associated with the biosynthetic fractionation factor for aquatic macrophytes. Usually, mid-chain n -alkanes such as $n\text{-C}_{23}$ are interpreted to be of aquatic origin, whereas the long-chain n -alkanes are interpreted to be of terrestrial origin. Given that (i) we found hardly any mid-chain n -alkanes in our archive and (ii) focus on the long-chain n -alkanes, we consider aquatic macrophytes to be of minor relevance in the case of our Gemündener Maar $\delta^2\text{H}_{n\text{-alkane}}$ record.

In our opinion, the issue raised by A. Lücke is much more problematic and may lead to erroneous interpretations when using $\delta^2\text{H}$ of $n\text{-C}_{23}$ for reconstructing $\delta^2\text{H}_{\text{lake-water}}$ (cf. “dual biomarker approach” of Rach et al., 2014, 2017), because Aichner et al. (2018) have recently shown for a lake in Poland that $n\text{-C}_{23}$ is a variable mixture of aquatic and terrestrial origin during the Late Glacial and Early Holocene. Namely, birch as pioneering and one of the dominant tree species during Late Glacial reforestation of Central Europe is known to produce considerable amounts of mid-chain n -alkanes (Tarasov et al., 2013). Albeit not included in the latter publication, $n\text{-C}_{23}$ concentrations of *Betula exilis* and *Betula pendula* reached 653 and even 2323 $\mu\text{g/g}$.

In the course of the YD- Holocene transition changes in precipitation isotopic composition have to be taken into account that will eventually translate into isotopic changes of source water (soil

water, shallow groundwater) utilized by terrestrial vegetation. How would those changes impact on the reconstructed d-excess values?

→ Yes, the YD-Holocene transition is indeed characterized by a shift towards more positive $\delta^2\text{H}/\delta^{18}\text{O}_{\text{source-water}}$ values as reconstructed by our coupled $\delta^2\text{H}_{n\text{-alkane}}-\delta^{18}\text{O}_{\text{sugar}}$ approach and as it can be expected. We will readily include this record in the revised manuscript. Importantly, however, the deuterium-excess variability of Greenland ice cores does not exceed 4‰ in the here relevant time period (see last paragraph of Chapter 3.3). Changes in $\delta^2\text{H}/\delta^{18}\text{O}_{\text{precipitation/source water}}$ have therefore a negligible effect on reconstructed d-excess and RH values.

Direct comparison of station data with reconstructed RH seems difficult as the amplitude of station Rh data in monthly means is driven by the seasonal cycle whereas the reconstructed Rh values represent massively smoothed multiannual / multidecadal means (Fig. 5).

→ Please note that our coupled $\delta^2\text{H}_{n\text{-alkane}} - \delta^{18}\text{O}_{\text{sugar}}$ paleohygrometer approach reconstructs daytime RH values for the vegetation period (therefore abbreviated RH_{dv}) (cf. also Tuthorn et al., 2015). We therefore consider the comparison with station RH data, calculated using monthly means from April to October between 6 a.m. and 7 p.m. from 1995 to 2015, to be appropriate.

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