

## ***Interactive comment on “Technical Note: *n*-Alkane lipid biomarkers in loess: post-sedimentary or syn-sedimentary?” by M. Zech et al.***

**M. Zech et al.**

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We are very grateful for your comprehensive and constructive review and feel that both your general and specific comments are valuable contributions to the discussion of our manuscript and help improving our manuscript.

Replies to general comments:

In your general comment 1 you address an issue, which was also raised by Dr. Yoshito Chikaraishi in his referee comment. We acknowledge that compound-specific  $^{14}\text{C}$ -dating of individual *n*-alkane homologues (as suggested firstly by T. Eglinton et al., 1996, *Anal. Chem.*) is the more sophisticated method than bulk *n*-alkane fraction  $^{14}\text{C}$ -dating. Nevertheless, you might agree that both methods have their advantages and

C3277

disadvantages (see our reply to Dr. Chikaraishi) and that even if using “only” bulk *n*-alkane fraction  $^{14}\text{C}$ -dating our study is highly innovative. To the best of our knowledge, it is the first study applying  $^{14}\text{C}$ -dating of biomarkers in loess, although Y. Huang et al. (1996, *Org. Geochem.*) and Rethemeyer et al. (2004, *Radiocarbon*) have already demonstrated that dating bulk *n*-alkane fractions is a powerful tool in biogeosciences. The fact that compound-specific  $^{14}\text{C}$ -dating is very challenging may help explaining why there are still hardly any studies published using this technique for dating of individual *n*-alkane homologues (Kusch et al., 2010, *GCA*). We agree that the *n*-alkane fraction comprises various sources. You have mentioned leaf waxes, roots (their *n*-alkane pattern show large variability, see X. Huang et al., 2011, *Geochem. J.*, cited on p.9879, l.3), charred OM (organic matter) and unknown origin. But we do not fully agree that these endmembers represent a multitude of varying  $^{14}\text{C}$  concentrations. Admittedly somewhat simplified, we rather suggest they either feature a syn-sedimentary age (this also holds true for charring-derived UCM, we do not consider it to be radiocarbon-dead) or a post-sedimentary age. Given that the post-sedimentary contamination is of unknown age, we carried out the mass balance calculation for different contamination scenarios (modern, current, 3, 6 and 9 ka BP, see Table 2). As we already replied to Dr. Chikaraishi, we agree that the UCM introduces an uncertainty, which is however difficult to quantify using the bulk *n*-alkane approach. We will include this in our revision.

In your general comment 2 you criticise the mass balance calculation approach for estimating the post-sedimentary *n*-alkane contamination. We admit that estimating  $^{14}\text{C}/^{12}\text{C}$  isotope ratios from an absolute optically stimulated luminescence (OSL) age has to be considered with caution. Anyway, it is at the same time without alternative in our opinion. An independent syn-sedimentary C-source (you suggested that possibly syn-sedimentary carbonates may help solving the problem) does not exist to the best of our knowledge. Your requested major revisions would lead to a non-quantitative assessment. We cannot agree, because apart from carrying our biomarker-specific  $^{14}\text{C}$ -dating in loess, the suggested quantitative estimation using the  $^{14}\text{C}$ -mass bal-

C3278

ance calculation is the innovative and crucial part of our study. Therefore we suggest including the following statement in the revised manuscript: "Calculating isotope ratios from OSL ages according to equation 1 should, methodologically, be considered with caution. However, so far it is without alternative and therefore intended as a first approximation."

In your general comment 3 you ask for the consequences of reworking for both radiocarbon and OSL ages and you ask for an explanation for higher abundances of mid-chain n-alkanes in the samples 15 and 19. On page 9884, line 6ff we explain that "...below 7.8m depth, the loess-paleosol sequence of Gleina is partly affected by deposition of reworked, older soil material. On the one hand, this could result in "too old" radiocarbon ages for the dated n-alkane fractions provided that the reworked soil material contained significant amounts of n-alkanes. Yet, M. Zech et al. (2012b) found that particularly the Eemian soil horizons of both the Gleina and the Nussloch (W-Germany) loess-paleosols sequences are characterised by extremely low n-alkane concentrations. On the other hand, deposition of reworked sediments may have implications for the interpretation of luminescence data when reconstructing the sedimentation history of loess-paleosol sequences due to insufficient signal resetting, which may cause discrepancies between the  $^{14}\text{C}$ - and OSL-derived ages.". On page 9883, line 12ff we further state that "In sample 15 additionally n-C21 and n-C22 [occur in relatively high amounts] (Fig. 1). While these n-alkanes typically do not occur in higher plant leaf waxes or at least in very low concentrations, Wiesenberg et al. (2009) showed that charring of grass biomass at 400 to 500 °C produces exactly such n-alkane patterns.". Please let us know if you think that further explanations are necessary.

In your general comment 4 you ask for a discussion of how the post-sedimentary n-alkane contamination occurs. While "...n-alkanes are hydrophobic [and therefore] not dissolved in and leached by soil water." (p.9878, l.28f), they occur at low concentrations in roots. Roots can penetrate loess several meters deep. Thus they introduce post-sedimentary root-derived n-alkanes, which may be partly preserved even if most of the

C3279

root organic matter is mineralised after the roots had rotted. Please let us know if you think this has to be included in the revised manuscript.

Replies to specific comments:

Where possible, we will include your requested corrections and suggestions during the revision. Additionally, we feel that the following comments deserve to be addressed in this reply.

p.9878, l. 25-26 and p.9883, l. 10-11: You recommend including a more detailed discussion about the average chain length, the dominating n-alkane homologue and the possibility to infer C3-C4 metabolic pathway changes. A detailed respective discussion and paleovegetation reconstruction were provided recently by Zech et al. (2012, *Quat. Int.*). We prefer not to include this in the revision, because it is out of the scope of our contribution. Similarly, we prefer not to discuss the aspect of metabolism by using the bulk n-alkane fraction  $\delta^{13}\text{C}$  results. It is widely accepted that in our study area C4 grasses did not significantly expand during the last glacial period.

p.9881, l. 1-4: We are very grateful for your suggestion to use urea adduction to remove the UCM. This was not done in our study but we suggest including and recommending this possibility in the revised manuscript and for future studies. Given that the UCM mostly likely derives from biomass burning/charring and/or from soil organic matter degradation, we do not think it is radiocarbon-dead, but rather suggest it has a syn-sedimentary age. Unfortunately, we do not see how we can reliably address the uncertainty caused by the UCM in our mass balance calculation (see our reply to general comment 1).

p. 9881, l.10-11: You ask for uncertainties of each measurement, doubt that solvent-derived carbon can explain a contamination with modern C and ask for potential n-alkane losses during the ethanol washing step. Readily, we will include uncertainty values of the  $^{14}\text{C}$  measurements in the revised Table 1. Concerning your assumption that a varying minor contamination with modern carbon might be introduced during

C3280

sample processing (e.g. CO<sub>2</sub> during gas handling), we think this can be excluded. The procedure of CO<sub>2</sub> gas handling is identical for all samples/standards in the Poznan Radiocarbon Laboratory and ca. 200 coal background samples during the last year never yielded <sup>14</sup>C background values higher than 0.4 pMC. Nevertheless we take your concern very serious and a <sup>14</sup>C dating of the dichlormethane (DCM) used in our tests and for n-alkane transfer is currently in progress in order to verify or exclude a potential <sup>14</sup>C contamination by DCM. We have not checked for potential n-alkane losses during the ethanol washing step. However, given that n-alkanes are not dissolved in ethanol, we assume that this step does not include the risk of n-alkane losses.

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C3281