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

Anonymous Referee #2

Received and published: 9 August 2012

Zech et al. present a small set of 14C data from n-alkane fractions of a loess sequence (Gleina, Germany) accompanied with OSL data from surrounding depths in order to investigate the sedimentary chronology of biomarkers and loess deposition to eventually evaluate the use of n-alkanes as an autochthonous syn-sedimentary signal rather than allochthonous post-sedimentary contamination (by roots). Finally, Zech et al. use mass balance equations to calculate the amount of post-sedimentary contamination in their n-alkane fractions.

The data are new and original, while the organic geochemical methodology does not make use of state of the art instrumentation allowing for better constraints on endmember assignments, which is the overall purpose of the study. Most importantly, however, the authors follow a wrong approach when using mass balance calculations. Overall,

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the manuscript requires major revisions leading to a non-quantitative assessment of the data set. In order to warrant publication, I would encourage additional 14C measurements (if the samples contain other carbonaceous materials).

GENERAL COMMENTS

1) The authors use the n-alkanes fraction rather than compound-specific radiocarbon analysis, which could have very successfully been performed given the reported total n-alkanes concentrations of 500-2000μg. This leads to difficulties in the interpretation of the sources of the n-alkanes combining various endmembers. i) some n-alkanes supposedly derive from roots - although the authors acknowledge that n-alkanes in roots only occur in minor quantities, but still they use them as essentially root-derived when assessing the modern contamination (see comment #4). Which homologues are representative for root n-alkanes (reference)? ii) long-chain n-alkanes (leaf wax lipids) derive from aboveground plant parts iii) short-chain n-alkanes also derive from charred OM/black carbon iv) some minor peaks of unknown origin (branched, unsaturated?) Accordingly, the 14C concentrations of the n-alkanes fraction represent a multitude of endmembers of varying 14C concentrations, which could have been disentangled using a compound-specific approach. In particular, in the presence of (likely radiocarbon-dead) black carbon (UCM!) obscures the modern contamination when using mass balance calculations (irrespective of the OSL absolute age, see comment #2).

2) The biggest pitfall of this manuscript is the wrong approach the authors take for their mass balance calculations of the modern contamination. The authors use the obtained OSL absolute ages to calculate isotope ratios (equation 1). This is not justifiable! Radiocarbon concentrations (measured as 14C/12C isotopic ratios) can be calibrated into absolute ages by statistical means determining the probability distribution of a sample's 14C/12C ratio to an independently derived true age (expressed by confidence intervals). This statistical approach is required due to the fact that atmospheric 14C concentrations have changed through time and given 14C/12C ratios might find var-

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ious calibrated age ranges. Accordingly, due to the atmospheric 14C concentration changes, it is not possible to assign or calculate an isotopic ratio from an absolute age! Such an isotopic ratio is, however, required in order to use mass balance calculations for calculating post-sedimentary n-alkane contamination. This can only be achieved if the authors analyze radiocarbon concentrations of an independent C-source (e.g. carbonates, if existing and syn-sedimentary), which then can be used in their mass balance calculations (due to the normalization of all 14C/12C ratios to a δ13C values of -25‰. Accordingly, the current data set can only be used for relative assessments of post-sedimentary contamination and for absolute quantitative evaluations.

3) Another poorly addressed topic is the fact that the age difference between OSL and calibrated 14C age is most prominent in the reworked section of the sequence. While sample 15 is younger than surrounding OSL dates and sample 19 lies within the error margins of both methods, samples 21 and 23 both are from the reworked sequence section. What do the authors attribute the reworking to (biotic or abiotic?) and what is the consequence of reworking for both the radiocarbon concentrations and the OSL ages? For these 2 samples also the chromatograms (short- and mid-length n-alkanes) differ from those of samples 15 and 19. The authors should address this issue.

4) One aspect I am missing is the discussion of how the authors believe the process of post-sedimentary contamination occurs. How do relatively younger n-alkanes get into deep loess profiles, if apparently they hardly occur in roots and are not easily transported in pore waters?

SPECIFIC COMMENTS

p. 9878, l. 16-17: I assume the authors refer to the average chain length of plants with C3 vs. C4 metabolic pathways? To my knowledge this is rather a dominance of n-C29 and n-C31 in C3 plants (not n-C27 and n-C29) vs. n-C31 and n-C33 in C4 plants. Specify and provide references.

p. 9878, l. 25-26: can you cite a published paper?

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p. 9880, l. 21-23: specify blank samples – also n-alkanes fraction? (I assume so referring to Table 1)

p. 9881, l. 1-4: Did the authors use urea adduction to remove the UCM apparent in the chromatograms shown in Figure 1? If not, this adds another (fossil black carbon?) endmember to potential mass balance calculations (given independent 14C age measurements) when estimating % post-sedimentary contamination in the n-alkane fractions, which needs to be addressed. This itself will require a justifiable method quantifying the UCM contribution to the n-alkane fractions.

p. 9881, l. 10-11: I don't agree with this statement. Most importantly, are the reported differences statistically significant? What are the uncertainties (2σ) of each of the measurements? Solvent-derived blank C should actually be radiocarbon-dead. The pMC differences reported for coal and the permafrost paleosoil samples might therefore rather be the result of varying minor contamination with modern C during further processing (e.g. CO_2 during gas handling). In particular, this is emphasized by sample Sib2, which was only transferred using DCM but in fact shows the least enriched pMC value. Also, sample "Bckg+DCM" seems to have been analyzed twice and both results yield 1pMC difference, but the $\delta13C$ values differ extremely. This strongly points to a different source of the observed modern contamination if it was derived from the DCM the stable isotope values should be rather similar. Could the authors comment on potential n-alkane loss during the ethanol washing step - did GC-FID quantification correspond to the CO_2 yields?

p. 9882, l. 3: delete "so-called"

p. 9883, l. 10-11: see specific comment #1; n-C31 is abundant in both classes and its co-abundance with n-C29 vs. n-C33 determines the metabolism. In this case, the relative peak intensity is higher for n-C29 pointing more towards the C3 metabolism, however, the actual peak areas might tell different. ACL is probably not the most robust proxy at all, the authors could discuss the aspect of metabolism by also using their bulk

n-alkane fraction δ13C results.

p. 9885, l. 11: delete "for"

p. 9885, l. 13-14: judging from the preservation of early MIS loess should it read "increased" rather than "limited preservation"? And what special morphographic position do the authors refer to?

p. 9885, l. 17-18: delete last sentence, repetitive

p. 9886, l. 7: re-name "current" vs. "modern". In the radiocarbon terminology "modern" refers to your "current". Use "decadal", "bomb-14C maximum" or any equivalent for your "modern" pool.

Table 1: provide explanations for abbreviations in table caption. What is "Bckg"?

Table 1 and 2: provide pMC and δ13C (also provide method for stable isotope measurements in respective section) errors

Table 2: add depths of samples, it is hard to guess that from Figure 1

Figure 1: where possible increase font size

Interactive comment on Biogeosciences Discuss., 9, 9875, 2012.