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

G. Wiesenberg
guido.wiesenberg@geo.uzh.ch

Received and published: 24 August 2012

The authors describe an approach to reconstruct the sources of alkanes in loess based on fraction-specific 14C dating.

By reading the manuscript I became aware of several aspects that need further consideration.

In the introduction the authors mention that alkanes are analysed in archives due to the ‘easy lipid extraction procedure’, which in fact is not true or only a minor part of the truth. First, e.g. cold water extracts would be much more easier, because one does not need a proper set-up. Second, alkanes were found to be of chemotaxonomic significance in plant leaves (e.g. several papers by Maffei and Maffei et al.) and in sedimentary environments they were described to be of diagnostic value (e.g. Schwark et al.), therefore highlighting their significance. Third, they were assessed due to their assumed high recalcitrance and probability to be preserved in sedimentary and terrestrial archives (e.g. Kuder & Krüge and Xie et al.) and therefore assumed to reflect paleoenvironmental changes.

The authors are simply wrong, if they describe their own publication (Zech et al. 2011b) as the first one performing biomarker research on loess-paleosol sequences. Numerous studies have been performed on the Chinese Loess Plateau, starting (to the best of my knowledge) with Jia et al. in 1987 – already 25 years b.p. and have been continued until the recent past (like Bai et al., Xie et al. and others).

The argument that GDGTs in loess-paleosol sequences are not contaminated by post-sedimentary microbial activity is also not completely valid as another publication than Zech et al., but from Huguet et al. showed exactly the opposite in the vicinity of former roots in loess.

The next problem I observed was the argumentation regarding $n$-alkanes in roots. First, alkane concentrations can be higher in roots than in aboveground plant tissues – there are several publications available on this. Also the already cited reference Huang et al describes for some species higher and for other lower amounts of alkanes in roots when compared to shoot tissues (e.g. Carex and Polygonum species). Second, in addition to the alkane content that is measured in roots, the authors also ignore rhizosphere processes at all (compare Jones or other reviews). Roots are continuously active during their growth, releasing exudates, producing fine roots (which commonly die rather quickly and might not be visible any more shortly after their death) and also release particulate organic matter into the soil or sediment. When only roots are analysed, one does not get an idea regarding the released substrates, which can also contain alkanes (like fine roots or particulate matter), whereas it is clearly documented in several publications that especially young plant tissues are enriched in alkanes. As fine roots are not easy to see (and even their remains are harder to see, probably with-
out leaving e.g. pores in the sediment), it is very hard to clearly state: our sediment we sample is definitely free of any postsedimentary root remains. Furthermore, the authors forget about the probability that alkanes are released if other components of roots like e.g. suberin, fatty acids, alcohols or others degrade. Some of the mentioned components can be also transferred in watery solutions (like exudates are) until a large distance from the former roots and release some alkanes there.

Regarding the comment by Chikaraishi and the anonymous reviewer, I agree that compound-specific 14C determinations are mandatory and probably also 14Corg measurements would be also useful, especially if short chain alkanes of another source than long chain alkanes are present. Otherwise, one gets only a mixed age, which tells not a lot. Investigation of other aliphatic compounds like hopanes, steranes, isoprenoidal alkanes and so on could contribute to a rough source assessment in the alkane fraction via GC/MS, which has not been performed. E.g. I see also pristane and phytane in the gas chromatogram, which can give some first insights into the degradation of the organic matter (see textbooks by Killops and Killops and Peters et al.). Furthermore, the authors state that investigations of other fractions than the alkane fraction should yield more results like fatty acids. As the lipid extraction procedure is 'easy' as they told in the introduction and they extract not only alkanes – why didn’t they analyse other lipids and PAHs, too? E.g. Rethemeyer et al. have also analysed 14C fraction-specific for different lipid fractions of the same sample and interpreted the results in terms of contamination and sources of organic matter within the fractions. Thus, it is surprising, why only part of the work has been done here.

In terms of the analysed sample set, it remains questionable, why samples for 14C and OSL were not taken for the same depth (and partially for the same stratigraphic unit), but from different ones. This weakens the meaning of the results as the OSL ages show a large scatter and not a continuous increase between 2.5 and 8 m and e.g. for sample 21 it is not clear, which OSL age would be correct. Anyhow, for this sample, the interpolated line (how was it calculated?) does not get a reliable result. Probably, also in that depth identical OSL ages would be observed like for the OSL sample taken half a meter above, if one analyses them from the same depth.

In the results and discussion section the authors cite their own paper, when they relate C31 alkane as grass derived. First, Maffei and many others published numerous papers on that before, and also Maffei et al. observed that C31 is largely abundant in coniferous trees. Additionally, there are hundreds of other papers that describe the variability of alkanes in plant tissues and that there are numerous other plants than grasses, showing an enrichment of C31 alkanes.

Another comment regarding the source of organic matter in soil: The authors state that petroleum derived C cannot enter the soil, but exactly this was described by Lichtfouse in one of his publications and also others report such contaminations.

The approach using 14C ages or root remains from other areas for the calculation of post-sedimentary overprint in the Saxonian loess sequences is problematic. The best would have been to analyse a root from the same area and also its alkanes for 14C. Otherwise, the results on % overprint are somehow randomized. E.g. what would be the case, if rooting has occurred 15 kyears before present or 100 years before present? A kind of calibration curve (starting immediately after sedimentation and finishing today) would be the best approach to assess this, rather than using three randomly chosen values for the calculation. Also the probability of rooting during former periods of paleosol formation is possible and was completely ignored. One example on that: What would have happened, if during the period, where the gelic Gleysol at 4.2 m depth has developed, one period of rooting occurred and another one 3 kyears before present (or no rooting after 20 kyears at all)?

In general, root contamination is discussed to modify the alkane patterns in the mentioned profile, if 14C ages do not correlate with OSL ages. As in general I agree for profiles, where root contamination is proven (was not done for the profile), also other potential overprints are possible. One could be particulate transport through the pro-
file, where also soot particles can be translocated, which would explain also the short chain alkanes in the distribution pattern. Alternatively also penetrating soil solutions containing DOC (including fatty acids) can be translocated and then might have released short chain alkanes at a large depth. It is also possible that short chain alkanes can be dissolved and transported in aqueous solutions as documented by Ferguson et al.

Due to the abovementioned comments, I guess that not all of the conclusions can be confirmed by the data.

Unfortunately, I was named in the acknowledgements of the manuscript, although a proper discussion of the data and the drawn conclusions did not occur. Otherwise, some of the abovementioned comments should have been acknowledged by the authors by mentioning the critical points before submission.

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