



Letter to the Editor

Reconstruction of the late Quaternary paleoenvironments of the Nussloch loess paleosol sequence—Comment to the paper published by Zech et al., Quaternary Research 78 (2012), 226–235
Keywords:

 Degradation
 Rhizomicrobial input
n-Alkanes

The motivation of this letter is to add missing links in the argument in the mentioned paper with respect to degradation, particularly when normalizing alkane contents on mass. Further discussion concerns the presumably low post-sedimentary alteration of terrestrial sedimentary organic matter (OM) and paleosols, for example by roots.

Frequently, contents of organic compounds are normalized to dry weight of plant or sedimentary OM, as is also done by Zech et al. (2012). The investigated compounds are characterized by different stability in the environment (Kögel-Knabner, 2002; Amelung et al., 2008). Most plant components can degrade quickly after incorporation in soils and sediments (Marschner et al., 2008) and might slightly change their composition during degradation, as already observed for *n*-alkanes (Nguyen Tu et al., 2004, 2011; Zech et al., 2011). The potential of selective preservation of individual compounds (Lichtfouse et al., 1998) is related to their degradability, stability and environmental controls such as fast burial and/or O₂-limited conditions (Lehmann et al., 2002).

In our opinion, the degree of alkane degradation should be assessed via normalization on organic carbon (C_{org}) content instead of normalizing on dry weight. In theory, if degradation of the overall OM would be identical for all individual compounds, the ratio of a substance (class) to C_{org} would remain constant. But this is not true, as some compounds like alkanes get enriched in sedimentary OM due to selective preservation (Lichtfouse et al., 1998; Zonneveld et al., 2010). Furthermore, alkanes can also be released in sediments by de-functionalization of for e.g. fatty acids, alcohols or decomposition of other alkyl side chains from macromolecules (Shimoyama and Johns, 1972; Poynter and Eglinton, 1991). Degradation of alkanes is accompanied by an equilibration of the abundance of odd and even homologues, hence reducing OEP (odd-over-even predominance) values, which Zech et al. (2012) acknowledge by their modeling approach.

If the abundance of alkanes is normalized on plant biomass and mass of soil or sediment, the comparison between source (plant) and archive (soil/sediment) is unsuitable to trace degradation of OM or the input of plant-derived OM into soils or sediments. Mass-normalized contents of organic compounds do not provide information about the amount of OM incorporated into the investigated archive. For example, scarce litterfall of a deciduous tree with high alkane contents can entail lower alkane input into soil than coniferous trees or roots with a lower alkane content compared to aboveground biomass, but a higher incorporation rate. Therefore, it is required to normalize alkane contents on the C_{org} content instead of mass, which then could yield more information with respect to the degradation and plant source.

Numerous publications are available reporting root alkane data (Marseille et al., 1999; Jansen et al., 2006; Roumet et al., 2006; Gocke et al., 2011a; Huang et al., 2011). For roots, clear separation between plant- and microbial-derived alkanes is impossible, which can be addressed by the term 'rhizomicrobial' alkanes. They constitute a low portion of the root biomass (10⁰–10² µg g⁻¹) but can be of the same order of magnitude as soil or sediment OM (10²–10³ µg g⁻¹ C_{org}) when related to C_{org} content (Marseille et al., 1999; Roumet et al., 2006; Gocke et al., 2011a). In the herein discussed study, the whole discussion regarding rhizomicrobial overprint of loess OM is based solely on two locally collected root samples, which is insufficient for drawing general conclusions insofar as no statistical evaluation supports the statements. The low resolution of samples collected per stratigraphic unit, and the absence of discussion of literature on root alkanes, impede identification of the root overprint of sedimentary OM in the current study. For this, more samples per unit and replicate samples are required.

Besides recent roots, terrestrial sediments frequently contain carbonatic root features described, for example, as rhizoliths or nodules, which are also abundant at Nussloch (Antoine et al., 2001; Gocke et al., 2011b). These derive from Holocene vegetation. As the recent roots in the profile are comparatively fresh and the profile was cleaned before sampling, the ancient root features still remain, which likely overprinted the lipid composition of the sediment and paleosols.

Although the alkane concentration is higher in litter than in roots, the latter is in a similar range as that of sedimentary alkanes (Gocke et al., 2011a; Zech et al., 2012). Thus, roots and associated microorganisms remain a potential source of sedimentary OM. As root-derived OM is characterized by lower degradability than aboveground biomass (Mendez-Millan et al., 2010), this also argues for rhizomicrobial alkanes as potential source of OM in soils and sediments.

Apart from the general abundance of alkanes, the process of incorporation of rhizomicrobial-derived OM is completely different compared to that of aboveground biomass. While in non-tropical climates litterfall of aboveground tissues commonly occurs once a year, roots continuously release OM throughout the year. This is of special importance for fine roots (Gaudinski et al., 2010) characterized by high productivity due to successive formation of new tissues and simultaneous decay of other fine roots. Thus, the rhizomicrobial-derived OM contribution was frequently underestimated in the past (Rasse et al., 2005). Roots are discussed to incorporate rather large amounts of biomass and help to sequester C belowground (Kell, 2012). Taking this into account, roots can release large amounts of alkanes as particulate OM, which can exceed that of litter, especially in deep soil horizons. Root exudation as proposed by Zech et al. (2012) is unlikely due to hydrophobicity of alkanes (Ferguson et al., 2009). Rhizomicrobial alkane incorporation is of special importance for steppe grassland, where most of the plant biomass is located belowground (Verchot et al., 2006).

In summary, we agree with most of the presented findings. Regarding degradation and root overprint of sedimentary OM, however, further research is required to elucidate discrepancies determined in the current and other studies. Other biomarkers like fatty acids, alcohols, suberin might be useful to support the findings related to degradation

and rhizomicrobial input. Also, compound-specific radiocarbon dating could help assessing postsedimentary-incorporated OM, which integrates over several sources of different ages unless specific biomarkers (for example, roots vs. litter) are used.

References

- Amelung, W., Brodowski, S., Sandhage-Hofmann, A., Bol, R., 2008. Combining biomarker with stable isotope analyses for assessing the transformation and turnover of soil organic matter. In: Donald, L.S. (Ed.), *Advances in Agronomy*. Academic Press, pp. 155–250.
- Antoine, P., Rousseau, D.D., Zoller, L., Lang, A., Munaut, A.V., Hatte, C., Fontugne, M., 2001. High-resolution record of the last interglacial–glacial cycle in the Nussloch loess–paleosol sequences, Upper Rhine Area, Germany. *Quaternary International* 76–7, 211–229.
- Ferguson, A.L., Debenedetti, P.G., Panagiotopoulos, A.Z., 2009. Solubility and molecular conformations of *n*-alkane chains in water. *The Journal of Physical Chemistry. B* 113, 6405–6414.
- Gaudinski, J.B., Torn, M.S., Riley, W.J., Dawson, T.E., Joslin, J.D., Majdi, H., 2010. Measuring and modeling the spectrum of fine-root turnover times in three forests using isotopes, minirhizotrons, and the Radix model. *Global Biogeochemical Cycles* 24.
- Gocke, M., Pustovoytov, K., Kuhn, P., Wiesenberg, G., Löscher, M., Kuzyakov, Y., 2011a. Carbonate rhizoliths in loess and their implications for paleoenvironmental reconstruction revealed by isotopic composition: $\delta^{13}\text{C}$, ^{14}C . *Chemical Geology* 283, 251–260.
- Gocke, M., Kuzyakov, Y., Wiesenberg, G.L.B., 2011b. Differentiation of plant derived organic matter in soil, loess and rhizoliths based on *n*-alkane molecular proxies. *Biogeochemistry*. <http://dx.doi.org/10.1007/s10533-011-9659-y>.
- Huang, X., Wang, C., Zhang, J., Wiesenberg, G.L.B., Zhang, Z., Xie, S., 2011. Comparison of free lipid compositions between roots and leaves of plants in the Dajiuhe Peatland, central China. *Geochemical Journal* 45, 365–373.
- Jansen, B., Nierop, K.G.J., Hageman, J.A., Cleef, A.M., Verstraten, J.M., 2006. The straight-chain lipid biomarker composition of plant species responsible for the dominant biomass production along two altitudinal transects in the Ecuadorian Andes. *Organic Geochemistry* 37, 1514–1536.
- Kell, D.B., 2012. Large-scale sequestration of atmospheric carbon via plant roots in natural and agricultural ecosystems: why and how. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences* 367, 1589–1597.
- Kögel-Knabner, I., 2002. The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biology and Biochemistry* 34, 139–162.
- Lehmann, M.F., Bernasconi, S.M., Barbieri, A., McKenzie, J.A., 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. *Geochimica et Cosmochimica Acta* 66, 3573–3584.
- Lichtfouse, É., Chenu, C., Baudin, F., Leblond, C., Da Silva, M., Behar, F., Derenne, S., Largeau, C., Wehrung, P., Albrecht, P., 1998. A novel pathway of soil organic matter formation by selective preservation of resistant straight-chain biopolymers: chemical and isotope evidence. *Organic Geochemistry* 28, 411–415.
- Marschner, B., Brodowski, S., Dreves, A., Gleixner, G., Gude, A., Grootes, P.M., Hamer, U., Heim, A., Jandl, G., Ji, R., Kaiser, K., Kalbitz, K., Kramer, C., Leinweber, P., Rethemeyer, J., Schäffer, A., Schmidt, M.W.I., Schwark, L., Wiesenberg, G.L.B., 2008. How relevant is recalcitrance for the stabilization of organic matter in soils? *Journal of Plant Nutrition and Soil Science* 171, 91–110.
- Marseille, F., Disnar, J.R., Guillet, B., Noack, Y., 1999. *n*-Alkanes and free fatty acids in humus and A1 horizons of soils under beech, spruce and grass in the Massif-Central (Mont-Lozère), France. *European Journal of Soil Science* 50, 433–441.
- Mendez-Millan, M., Dignac, M.F., Rumpel, C., Rasse, D.P., Derenne, S., 2010. Molecular dynamics of shoot vs. root biomarkers in an agricultural soil estimated by natural abundance ^{13}C labelling. *Soil Biology and Biochemistry* 42, 169–177.
- Nguyen Tu, T.T., Derenne, S., Largeau, C., Bardoux, G., Mariotti, A., 2004. Diagenesis effects on specific carbon isotope composition of plant *n*-alkanes. *Organic Geochemistry* 35, 317–329.
- Nguyen Tu, T.T., Egasse, C., Zeller, B., Bardoux, G., Biron, P., Ponge, J.-F., David, B., Derenne, S., 2011. Early degradation of plant alkanes in soils: a litterbag experiment using ^{13}C -labelled leaves. *Soil Biology and Biochemistry* 43, 2222–2228.
- Poynter, J., Eglinton, G., 1991. The biomarker concept – strengths and weaknesses. *Fresenius' Journal of Analytical Chemistry* 339, 725–731.
- Rasse, D., Rumpel, C., Dignac, M.-F., 2005. Is soil carbon mostly root carbon? Mechanisms for a specific stabilisation. *Plant and Soil* 269, 341–356.
- Roumet, C., Picon-Cochard, C., Dawson, L.A., Joffre, R., Mayes, R., Blanchard, A., Brewer, M.J., 2006. Quantifying species composition in root mixtures using two methods: near-infrared reflectance spectroscopy and plant wax markers. *New Phytologist* 170, 631–638.
- Shimoyama, A., Johns, W.D., 1972. Formation of alkanes from fatty acids in the presence of CaCO_3 . *Geochimica et Cosmochimica Acta* 36, 87–91.
- Verchot, L., Krug, T., Lasco, R.D., Ogle, S., Raison, J., Li, Y., Martino, D.L., McConkey, B.G., Smith, P., Karunditu, M.W., 2006. Grassland. In: Eggleston, H.S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K. (Eds.), *Agriculture, Forestry and Other Land Use*. : IPCC Guidelines for National Greenhouse Gas Inventories, vol. 4. IGES, Japan, Hayama, Kanagawa.
- Zech, M., Pedentchouk, N., Buggle, B., Leiber, K., Kalbitz, K., Marković, S.B., Glaser, B., 2011. Effect of leaf litter degradation and seasonality on D/H isotope ratios of *n*-alkane biomarkers. *Geochimica et Cosmochimica Acta* 75, 4917–4928.
- Zech, M., Rass, S., Buggle, B., Löscher, M., Zöllner, L., 2012. Reconstruction of the late Quaternary paleoenvironments of the Nussloch loess paleosol sequence, Germany, using *n*-alkane biomarkers. *Quaternary Research* 78, 226–235.
- Zonneveld, K.A.F., Versteegh, G.J.M., Kasten, S., Eglinton, T.I., Emeis, K.-C., Huguet, C., Koch, B.P., de Lange, G.J., de Leeuw, J.W., Middelburg, J.J., Mollenhauer, G., Prahl, F.G., Rethemeyer, J., Wakeham, S.G., 2010. Selective preservation of organic matter in marine environments; processes and impact on the sedimentary record. *Biogeosciences* 7, 483–511.

Guido L.B. Wiesenberg

Department for Geography, University of Zurich,
Winterthurerstrasse 190, CH-8057 Zurich, Switzerland
Corresponding author. Fax: +41 44 635 6848.
E-mail address: guido.wiesenberg@geo.uzh.ch.

Martina Gocke

Department of Agroecosystem Research, University of Bayreuth,
95440 Bayreuth, Germany

15 November 2012