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Rhizoliths in loess – evidence for post-sedimentary incorporation of root-derived organic matter in terrestrial sediments as assessed from molecular proxies

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ABSTRACT

Loess–palaeosol sequences are important terrestrial archives for studying Quaternary climate change. A major assumption for palaeoenvironmental reconstruction based on loess organic matter (OM) is that it represents the signal of syn-sedimentary incorporated plant biomass, i.e. predominantly grass vegetation. However, recent studies on rhizoliths (roots encrusted by secondary carbonate) formed in loess reveal the possibility of post-sedimentary penetration of loess–palaeosol sequences by deeply rooting plants. This likely led to incorporation of younger root-derived OM into surrounding loess, potentially causing an overprinting of the initial plant-derived signal of loess OM.

To obtain information on the source vegetation of rhizoliths and surrounding loess OM we examined rhizoliths and loess from Nussloch, SW Germany, using alkane and fatty acid (FA) molecular proxies. Moreover, the lipid composition was compared in transects from rhizoliths via rhizosphere loess towards root-free loess for a preliminary assessment towards quantifying the post-sedimentary input of root-derived OM in loess.

Loess OM gave a combined signal from shoot and root biomass from grass vegetation, confirming the assumption of deposition during glacial periods with scarce grass vegetation cover. In contrast, the lipid composition of rhizolith OM reflected roots of woody vegetation, indicating the post-sedimentary character of rhizoliths. Stronger degradation of OM, together with a large content of microorganism-derived FAs in the former rhizosphere indicated rhizodeposition associated with high microbial activity in loess adjacent to rhizoliths, at least up to a distance of 5 cm. Rhizosphere loess and reference loess at a distance of 50–70 cm showed a significantly different OM composition, thereby revealing the incorporation of considerable portions of root-derived OM into loess in the vicinity of roots. Further studies are necessary for an exact quantification of this potential overprint of the syn-sedimentary loess OM, which might cause uncertainty in palaeoenvironmental studies.

1. Introduction

Soils of arid and semiarid regions show favourable conditions for precipitation of secondary carbonate (Birkeland, 1999), which takes place in isotopic equilibrium with soil CO_2 (Cerling, 1984) released by way of root respiration and organic matter (OM) decomposition. Rhizoliths are a particular form of secondary $CaCO_3$ formed by encrustation of plant roots. While the organic part of the root is mainly degraded during decomposition, tubular carbonatic structures remain in the sediment. They occur locally in sandy and silty calcareous sediments (Ziehen, 1980; Becze-Deák et al., 1997), usually separately from other types of secondary carbonate accumulations (Becze-Deák et al., 1997).

Rhizoliths were first mentioned as 'Osteokollen' [see review by Ziehen (1980)] because of their bone-like structure (Greek osteon = bone, Latin collon = stem). Due to the variability in their morphology and occurrence in a variety of different settings, numerous names have been used for rhizoliths [e.g. rhizocretion, root cast; summarized by Klappa (1980)] and distinct hypotheses for their genesis have been discussed. Calcified root structures can be a precursor of rhizogenic calcretes, i.e. calcretes formed mainly by root activity (Wright, 1989).

Rhizoliths have been frequently described. However, it is a somewhat novel approach to use them as a proxy for palaeoenvironmental reconstruction, although they are probably very sensitive environmental recorders (Becze-Deák et al., 1997). Such reconstruction based on calcified roots has focussed on the carbonate (carb) material, either by way of macro- and micromorphological studies (Becze-Deák et al., 1997; Alonso-Zarza and Arenas, 2004), or stable carbon and oxygen isotopic analysis ($\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$; Kuleshov and Gavrilov, 2001; Alonso-Zarza and Arenas, 2004; Pustovoytov and Terhorst, 2004; Wang and Greenberg, 2007).

The vegetation under which rhizoliths were formed has been scarcely examined. In some early studies, they were attributed exceptionally to coniferous trees, whereas others reported calcified

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roots additionally for other woody vegetation like peach and birch (Ziehen, 1980). Jaillard and Callot (1987) described recent calcified roots mainly under grassland and herbaceous plants, whereas they were rarely observed under pine and possibly under wine plants (B. Jaillard, personal communication). However, according to Ziehen (1980), determination of the source vegetation is impossible if the calcified roots are no longer connected to the plant. A preliminary source apportionment was tried on the basis of the shape and size of rhizoliths and root features in calcretes. For instance, Wright et al. (1988) concluded from the morphology of palaeosol calcretes from the UK and Spain that 'relatively small plants' prevailed during formation of the secondary carbonate concretions. Except for determination of the photosynthetic pathway of source vegetation of rhizoliths using $\delta^{13}C_{carb}$ (see above), to the best of our knowledge no further analytical methods have been performed, which focus on a more detailed characterization of the former vegetation. We hypothesize that part of the OM derived from root tissue must be preserved within and beneath rhizoliths in loess, because secondary carbonate encrustation leads to protection of organic remains from the former root tissue against degradation by microorganisms. The molecular composition of OM within rhizoliths should provide evidence of the former vegetation; to the best of our knowledge this has not been tested. Biomarker analysis using diagnostic molecular proxies could help determine the plant origin of OM because of their chemotaxonomic significance (Maffei, 1996a,b; Rommerskirchen et al., 2006; Wiesenberg and Schwark, 2006). Numerous organic compounds typical of individual plant species, e.g. suites of terpenes in pine trees, occur in plants. After plant death, degradation of biomass results in typical degradation products in soils and sediments, which can be used as biomarkers (Peters et al., 2005). For grass, such specific biomarkers have not been observed. Nevertheless, molecular proxies obtained from the distribution of fatty acids (FAs), alcohols and alkanes have been found to be of chemotaxonomic significance for differentiating grasses from woody plants (Maffei, 1996a,b), or among grasses following different photosynthetic pathways (C_3 vs. C_4; Rommerskirchen et al., 2006; Wiesenberg and Schwark, 2006). Alkanes in loess have in particular been used for source apportionment of the vegetation (Xie et al., 2003; Liu and Huang, 2008; Bai et al., 2009), but the approach has been rarely attempted with FAs and alcohols (Xie et al., 2003). Because of the presumed lower recalcitrance of FAs and alcohols (Bol et al., 1996; Wiesenberg et al., 2004b, 2008) in loess, when compared to alkanes, the number of studies is limited. Nevertheless, the cold and arid climatic conditions prevailing during loess accumulation enable good preservation of molecular proxies (Kuder and Kruge, 1998; Xie et al., 2004). Additionally, encrustation of root tissue by $CaCO_3$ provides improved preservation of OM in rhizoliths. In this study, we investigated for the first time lipids and molecular proxies deriving from FAs and alkanes in rhizolith OM and loess in Central Europe.

As rhizoliths occur in terrestrial sediments, it can be assumed that root-derived OM was incorporated during the lifetime of the roots in adjacent soil and sediment, the so called rhizosphere. This can be expected as the rhizosphere of living roots is a hot-spot of fine roots, root growth, and nutrient and water acquisition (Jones, 1998). Hence, close to large rhizoliths, residues of fine roots and root exudates, as well as associated microorganisms that lived in the former rhizosphere, can be expected. This has been ignored in past studies of loess–palaeosol sequences. While it was clearly shown that root exudates consist mainly of low molecular weight organic components (Bertin et al., 2003), it can be assumed that the recalcitrance of these organic compounds in loess–palaeosol sequences is limited as a result of their high solubility and susceptibility to being consumed by microorganisms. Hence, organic remains of microorganisms feeding on exudates rather than the exudates themselves might have the potential to be preserved in the former rhizosphere. While many authors suggest that rhizolith formation occurred syn-sedimentary with loess deposition (Becze-Deák et al., 1997; Wang and Greenberg, 2007), recent studies reveal that roots, as well as calcareous root features, in loess–palaeosol sequences can be significantly younger than surrounding loess (Pustovoytov and Terhorst, 2004). Hence, rooting of younger plants must have significantly changed the loess OM in the vicinity of the roots, not only by incorporation of root-derived OM itself, but additionally by cometabolic degradation of initial loess OM by microorganisms feeding on root exudates and root remains. However, the amount of post-sedimentary root-derived OM incorporated into terrestrial sediments is unknown. Particularly for Quaternary continental sediments with high chronological resolution, which are used for palaeoenvironmental reconstruction, this uncertainty can entail problems for the interpretation of the stable carbon isotopic composition of OM ($\delta^{13}C_{org}$) as a proxy for palaeovegetation, palaeoprecipitation and other palaeoecological conditions (e.g. Hatté and Guiot, 2005). Some authors have already mentioned the problem of post-sedimentarily incorporated biomass in terrestrial sediments (Head et al., 1989; Zhou et al., 2005). Attempts to correct the bulk organic signals are scarce (Liu et al., 2007) or resulted in fractionation of the bulk carbon pool and the assumption that only particulate OM (90–300 μm) reflects the original C_{org} signal (Head et al., 1989; Zhou et al., 2005). Most authors assume that OM enters buried terrestrial sediments mainly via dissolved organic carbon, whereas incorporation of root-derived OM has not been discussed. We hypothesize that a considerable amount of root-derived OM is incorporated into terrestrial sediments (e.g. loess) adjacent to roots and that this can be quantified by comparing the molecular composition of root and rhizosphere materials (remaining root biomass and organic material in the sediment) with that of sediments of the same horizon distant from roots.

In the region of Heidelberg, SW Germany, rhizoliths with a diameter of up to 5 cm occur locally abundant in dune sands at Sandhausen (Löscher and Haag, 1989), as well as in the loess–palaeosol sequence at Nussloch, with a high abundance in the Nussloch loess section (ca. 10–20 rhizoliths m^{-2}). These rhizoliths were formed by C_3 vegetation, as shown by the stable carbon isotopic composition of organic carbon ($\delta^{13}C_{org}$ −25.9 ± 0.5‰) and inorganic carbon ($\delta^{13}C_{carb}$ −10.9 ± 0.1‰; Gocke et al., unpublished results). So far, only one rhizolith radiocarbon age (3150 yr b.p.; Gocke et al., unpublished results) is available from Nussloch, indicating post-sedimentary formation of this rhizolith. However, rhizoliths from the same depth might have formed during different time intervals (Ziehen, 1980), thereby impeding general conclusions about the chronological context between terrestrial sediments and calcified roots. The aim of this study was to elucidate the origin of these rhizoliths using molecular markers. Comparison of the composition of lipid fractions in rhizoliths and loess parent material should provide information concerning the sources of both materials, thereby providing evidence whether rhizolith formation took place simultaneously with loess deposition or was a post-sedimentary occurrence. Moreover, we aimed to quantify the input of root-derived material to the rhizosphere. We therefore analysed several rhizoliths and horizontal transects from these rhizoliths to loess distant from roots for their molecular composition with respect to FAs and alkanes.

2. Materials and methods

2.1. Sampling

Rhizolith and loess samples were collected from a late Pleistocene loess–palaeosol sequence at the open cast mine of

HeidelbergCement AG, Nussloch, SW Germany (49.19°N, 8.43°E, 217 m above sea level) from a depth interval between 2.2 and 2.6 m below the present surface. The recent soil had a depth of 0.8 m, so samples were taken 1.4–1.8 m below the recent soil. The loess–palaeosol sequence, with a total thickness of 18.5 m, did not show any sign of recent pedogenesis in the sampled interval. Loess from the profile had a total organic carbon (C_{org}) content of < 5 mg g^{-1} and high C_{carb} content of 34 mg g^{-1} (Bente and Löscher, 1987), leading to a high pH ($CaCl_2$) of 8.1. For a more detailed description of the sampling site see Antoine et al. (2001). For two rhizoliths (R), loess transects were sampled from the former root (i.e. rhizolith) towards root-free loess at distances from 0–2.5 cm and 2.5–5 cm from R and were named rhizoloess (RL1 and RL2, respectively). Reference loess (L), which was free of any visible root remains, from the same depth interval and the same stratigraphic unit, was sampled at a distance of 50–70 cm from R. Both rhizoliths had a length of 20–40 cm, a diameter of 2–4 cm and were of similar morphology.

All replicate results in the following represent separate analyses of two different rhizoliths and corresponding transects towards reference loess.

2.2. Elemental and lipid analysis

Rhizoliths were rinsed with deionized water to remove adhering loess, and all samples were dried at 60 °C for 24 h and crushed in a ball mill. C_{org} and C_{carb} contents of rhizoliths and loess were measured by way of combustion in an oven (Feststoffmodul 1300, AnalytikJena) at 550 °C and 1000 °C, respectively, followed by CO_2 detection with a N/C analyser (AnalytikJena).

Loess (root-free loess, ca. 100 g; rhizoloess, 30–50 g) and rhizolith samples (30–50 g) were extracted for free lipids with dichloromethane (DCM)/MeOH (93:7, v:v; Wiesenberg et al., 2004a) using Soxhlet extraction for at least 40 h. Neutral and FA fractions were obtained by way of chromatographic separation of the extract using solid phase extraction (SPE) with KOH-coated silica gel (Wiesenberg et al., 2004a, 2010). Neutral lipids were eluted with DCM, followed by FAs, which were eluted with DCM/HCO_2H (99:1, v:v). After reducing the solvent volume to dryness, the neutral fraction was dissolved in hexane and separated with respect to aliphatic and aromatic hydrocarbons, as well as low polarity hetero compounds. Separation was performed on columns filled with activated silica gel (100 Å) by eluting aliphatic hydrocarbons with hexane, aromatic hydrocarbons with hexane/DCM (1:1, v:v) and low polarity hetero compounds with DCM/MeOH (93:7, v:v). The FA and aliphatic hydrocarbon fractions in particular afforded interesting results from gas chromatography with flame ionisation detection (GC–FID; Agilent 7890) after addition of deuteriated standards for quantification ($D_{39}C_{20}$ acid, or $D_{50}C_{24}$ alkane, respectively). FAs were derivatized using BSTFA [*N,O*-bis(trimethylsilyl)trifluoroacetamide] prior to GC, while aliphatic hydrocarbons were directly amenable to GC–FID analysis. Identification of compounds and determination of possible co-elutions were performed via GC–mass spectrometry (GC–MS) analysis (HP 5890 chromatograph coupled to a HP 5971spectrometer) and correlation with external standard mixtures.

2.3. Molecular proxies

2.3.1. Carbon preference index

Long chain FAs in fresh biomass from higher plants typically reveal a strong predominance of even homologues (Tissot and Welte, 1984), expressed in the carbon preference index (CPI_{FA}):

$$CPI_{FA} = \left[\left(\sum n\text{-}C_{20-32\ \text{even}} \Big/ \sum n\text{-}C_{19-31\ \text{odd}}\right) + \left(\sum n\text{-}C_{20-32\ \text{even}} \Big/ \sum n\text{-}C_{21-33\ \text{odd}}\right)\right] \Big/ 2 \quad (1)$$

While fresh plant biomass usually has CPI_{FA} values > 4, degradation after sedimentation and microbial reworking result in values close to 1 (Cranwell et al., 1987), because of preferential decomposition of even homologues and a contribution from odd homologues, e.g. of wax esters or other potential precursor compounds with long chain alkyl FAs, during degradation.

The CPI for alkanes (CPI_{Alk}) has a similar meaning to CPI_{FA}, except it relates to a predominance of odd homologues and contains primary wax remains of plants as well as degradation products of different compound classes including, e.g. alcohols, FAs and wax esters:

$$CPI_{Alk} = \left[\left(\sum n\text{-}C_{25-35\ \text{odd}} \Big/ \sum n\text{-}C_{24-34\ \text{even}}\right) + \left(\sum n\text{-}C_{25-35\ \text{odd}} \Big/ \sum n\text{-}C_{26-36\ \text{even}}\right)\right] \Big/ 2 \quad (2)$$

Odd *n*-alkanes are dominant components of plant leaf waxes (Eglinton et al., 1962; Kolattukudy et al., 1976), whereas even homologues derive mainly from degradation of OM. Degradation of plant OM results in a decrease in the odd predominance (Zhou et al., 2005). CPI_{Alk} values <10 indicate degradation of OM (Cranwell, 1981) or can be related to root biomass (Wiesenberg et al., unpublished results). In addition, microbial OM contains mainly short chain alkanes and lacks an even or odd predominance. Therefore, CPI_{Alk} values around 1 are characteristic of highly degraded OM and/or abundant microbially-derived OM (Cranwell, 1981; Zhou et al., 2005).

2.3.2. Average chain length (ACL)

The ACL of FAs (ACL_{FA}) indicates whether OM in sediments is derived predominantly from microbial (values < 20) or plant biomass (values > 20), because long chain FAs (> C_{20}) are produced exclusively by plants, whereas short chain FAs can be derived from plants and microbial biomass (Kolattukudy et al., 1976). ACL_{FA} is calculated as follows:

$$ACL_{FA} = \sum(z_n \times n) \Big/ \sum(z_n) \quad (3)$$

where n is the number of carbons and z_n the amount of the FA with n carbons, with n in the range 12–32.

Analogous to ACL_{FA}, the ACL of alkanes (ACL_{Alk}) indicates the degradation of plant and microbial biomass as well as microbially-derived OM (Bray and Evans, 1961). The contribution of long chain plant-derived components is indicated by high values $\geqslant 23$ (Eglinton et al., 1962; Kolattukudy et al., 1976), while the presence of microbially-derived OM is expressed by lower values. ACL_{Alk} is calculated as

$$ACL_{Alk} = \sum(z_n \times n) \Big/ \sum(z_n) \quad (4)$$

where n is the number of carbons and z_n the amount of alkanes with n carbons, with n in the range 12–15.

2.4. Statistical analysis

Mean values and standard errors of the mean are presented for replicate analyses. Differences between rhizolith, rhizoloess and loess were tested to be significant using a *t*-test for dependent samples with a significance level of $\alpha = 0.1$. Statistical analysis was carried out using STATISTICA for Windows (version 7.0, StatSoft Inc., Tulsa, USA).

3. Results and discussion

3.1. Bulk carbon and lipid content

The C_{org} content decreased strongly from 72 ± 9 mg g^{-1} in rhizoliths (R) to 10 ± 1 mg g^{-1} in rhizoloess (RL) 1 and 6 ± 1 mg g^{-1}

in RL2. The C_{carb} content was 92 ± 2 mg g^{-1} for R, but only 46 ± 1 mg g^{-1} for RL 1 and 44 ± 1 mg g^{-1} for RL2 (corresponding to $CaCO_3$ contents of 76 ± 1%, 38 ± 0.4% and 37 ± 0%). C_{org} and C_{carb} contents of reference loess (L) were slightly lower (4 ± 2 mg g^{-1} and 40 ± 3 mg g^{-1}, respectively; Fig. 1A) than the RL values, without significant differences between RL and L.

The extractable lipid content normalized to sample weight was 168 ± 13 μg g^{-1} for R and immediately dropped towards 62 ± 5 μg g^{-1} for RL. For all RL samples the extractable lipid content was almost identical. For L the lipid content was lowest (48 ± 7 μg g^{-1}), but did not significantly differ from RL (Fig. 1B). The lipid content of all samples was lower than that of recent surface soils (ca. 300–600 μg g^{-1}; Amblès et al., 1994; Lichtfouse et al., 1995; Wiesenberg et al., 2006), but almost comparable to B horizons of recent soils (20–90 μg g^{-1}; Wiesenberg et al., 2006). The lower lipid content of loess can be attributed to the generally low content of OM in loess. At Nussloch, C_{org} content of rhizoloess, as well as reference loess sampled at a distance of 50–70 cm from the rhizolith, was between 4 and 10 mg g^{-1}, which is in a similar range to literature data from Nussloch (5 mg g^{-1}; Bente and Löscher, 1987). The content of extractable lipids of R was 2.5 times as high as for RL and three times as high as for L (Fig. 1B). This is attributed mainly to larger initial input of OM in rhizoliths by way of root growth when compared to loess, which contains OM from a presumably sparse grass vegetation cover present during deposition (Bai et al., 2009). Additionally, encrustation of the root tissue by secondary carbonate might have led to improved preservation of root material.

Normalized to C_{org} content, the amount of extractable lipids was lowest in R (2.4 ± 0.1 mg g^{-1} C_{org}), increased in RL (6.9 ± 1.4 mg g^{-1} C_{org} in RL1 and 10.9 ± 1.2 mg g^{-1} C_{org} in RL2) and was highest in L (106.5 ± 51.7 mg g^{-1} C_{org}; Fig. 1B). Extractable lipids comprised 1–2% of total biomass for fresh root tissue (ca. 2.2–4.4% of C_{org}; Wiesenberg, 2004 and unpublished data), whereas the portion was considerably higher for above-ground plant parts (4–10% of biomass or ca. 8.9–22.2% of C_{org}; Wiesenberg, 2004; Wiesenberg et al., 2008 and unpublished data). This suggests that lipids in rhizoliths and rhizoloess might be of root origin, with a very low contribution from extractable lipids and preservation of more complex OM structures including, e.g. lignin (Marschner et al., 2008). In contrast, the highest lipid contents related to C_{org} in loess indicate above- and below-ground biomass as the source for loess OM. The large contribution of extractable lipids to C_{org} in loess (106.5 ± 51.7 mg g^{-1}) is even larger than for recent soils (Wiesenberg et al., 2006) and is related to the strong degradation of precursor compounds since sedimentation, which is connected with a selective enrichment in degradation products like alkanes (see below).

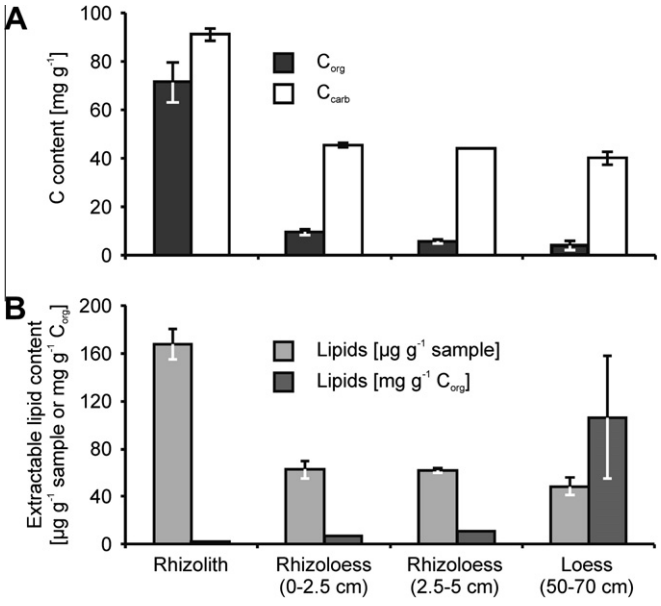

Fig. 1. Content of (A) C_{org} and C_{carb} and (B) extractable lipids in rhizolith, rhizoloess and loess. Lipid content was normalized to bulk sample and C_{org}. Distance of loess samples from rhizoliths is given in parentheses.

3.2. Molecular composition

Besides distribution patterns of FAs and alkanes, several molecular proxies were found to be useful in elucidating the source of the OM in loess, rhizoloess and rhizolith samples. They include the sum of mono-unsaturated FAs (MUFAs; $C_{14:1}$, $C_{16:1}$, $C_{18:1}$), the sum of poly-unsaturated FAs (PUFAs; $C_{16:2}$, $C_{18:2+3}$), the preference of even/odd long chain FAs (CPI_{FA}), the preference of odd/even long chain alkanes (CPI_{Alk}) and ACL_{FA} and ACL_{Alk}.

3.2.1. FAs

Distribution patterns of FAs in both loess and rhizolith samples showed a dominance of $C_{16:0}$ and long chain homologues (> $C_{17:0}$), as well as a predominance of even/odd long chain FAs. Rhizosphere loess distribution patterns were similar to those of R and L, but lacked long chain homologues > $C_{25:0}$ (Fig. 2). In general, the FA distributions confirmed the composition of plant-derived OM in terrestrial environments (Xie et al., 2003). This was confirmed by high CPI_{FA} values in L (4.0 ± 0.5) and R (7.6 ± 1.2). Significantly lower ($p < 0.05$) CPI_{FA} values were obtained for RL (1.7 ± 0 in RL1 and 1.4 ± 0 in RL2), indicating a stronger degradation and/or microbial remains dominating the source of the FAs in the rhizosphere.

$C_{14:1}$ and $C_{16:1+2}$ unsaturated FAs are mainly attributed to microbial OM (Kolattukudy et al., 1976; Harwood and Russell, 1984). The contribution of these components to total FAs increased from rhizolith (8.3 ± 1.6%) to loess adjacent to rhizoliths (0–2.5 cm; 11.5 ± 1.8%) and decreased at a larger distance towards the reference loess (rhizoloess 2.5–5 cm: 4.4 ± 0.5%; loess: 1.6 ± 0.4%; Fig. 3). Poly-unsaturated $C_{18:2+3}$ and long chain FAs ($\geqslant C_{20:0}$) are attributed to higher plant-derived OM (Kolattukudy et al., 1976; Harwood and Russell, 1984) and contributed most to the total FAs in rhizoliths (48.0 ± 2.0%). These contributions were significantly lower ($p < 0.005$) in rhizoloess (0–2.5 cm: 19.4 ± 3.5%, 2.5–5 cm: 21.7 ± 1.6%, respectively) than in rhizoliths. In loess the contribution of these plant-derived FAs was in a similar range as in rhizoliths (46.2 ± 11.7%). In particular, the abundance of PUFAs successively decreased with increasing distance from rhizolith (5.8 ± 0.1%) towards reference loess (0%). The remaining short chain FAs ($C_{12:0-19:0}$, $C_{18:1}$), attributed to both microbial and higher plant biomass (Kolattukudy et al., 1976), increased from rhizoliths (43.6 ± 3.8%) to rhizoloess (0–2.5 cm: 69.0 ± 5.3; 2.5–5.0 cm: 73.9 ± 2.1) and dropped towards reference loess (52.1 ± 11.3%).

The FA distribution of rhizolith OM, with a high abundance of $C_{16:0}$ and low abundance of very long chain homologues (> $C_{26:0}$), with the exception of very high amounts of $C_{30:0}$, might indicate its root origin, as suggested by the morphology (Klappa, 1980; Ziehen, 1980). Even long chain FAs (> $C_{19:0}$) were most abundant in loess, except for $C_{30:0}$, which showed much higher content in R than L. The most abundant long chain FA was $C_{28:0}$ in L, but was $C_{24:0}$ in rhizoloess and $C_{30:0}$ in rhizolith samples. Therefore, the contribution of plant-derived biomass and/or its corresponding degradation remains must be different in these sample types. Most likely, the large increase in $C_{24:0}$ FA from L towards RL derives from rhizodeposits in the vicinity of roots and/or more intensive degradation of plant biomass than in loess and rhizolith. This is confirmed by the high abundance of microorganism-derived FAs in the rhizoloess as, indicated by MUFA, CPI_{FA}, and additionally exceptional low values of ACL_{FA}.

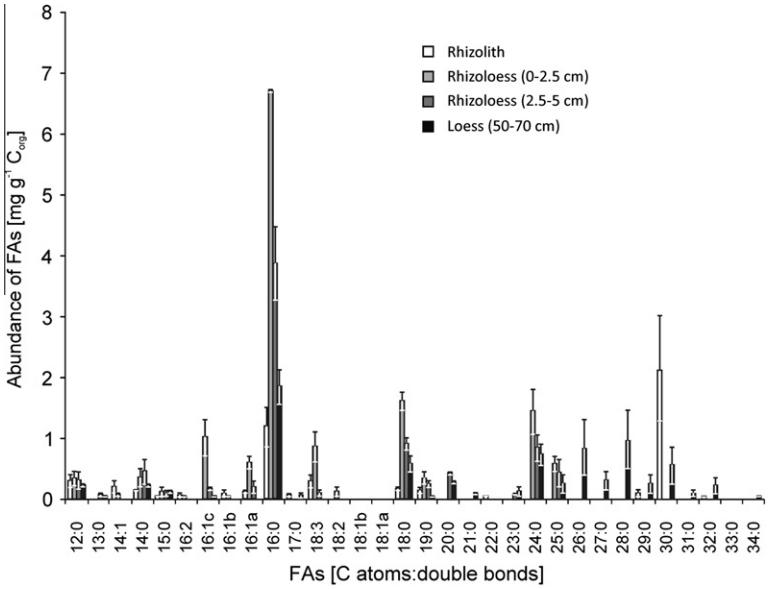

Fig. 2. FA distribution in rhizolith, rhizoloess and reference loess; FA amount is normalized to C_{org} (mg g^{-1} C_{org}).

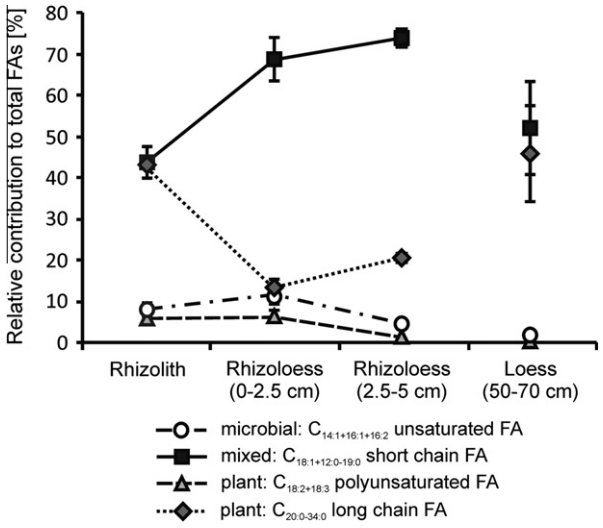

Fig. 3. Relative contribution of FAs of different origin (microbial and higher plant as well as mixed sources) to total FA fraction for rhizoliths and corresponding transects via rhizoloess towards reference loess.

Like CPI_{FA} (Fig. 4A), ACL_{FA} values were highest in R (21.8 ± 0.4) and slightly lower in L (20.3 ± 1.6), with RL samples having the lowest values (17.8 ± 0.3 in RL1 and 17.6 ± 0.1 in RL2; Fig. 4B). While fresh plant biomass is commonly characterized by high ACL_{FA} and CPI_{FA} values, degradation results in decreasing values (Peters et al., 2005). Additionally, the contribution of microbial biomass itself and of microbial reworking is expressed in very low ACL_{FA} and CPI_{FA} values (Cranwell, 1981). Hence, the highest CPI_{FA} and ACL_{FA} values for R are related to plant-derived OM, which is less degraded than the OM in L with intermediate values. The very low CPI_{FA} and ACL_{FA} values in RL are attributed to the relatively high abundance of microbially-derived OM near R, i.e. in the former rhizosphere, as previously described only for recent soils and living plants (Jones, 1998). As the former rhizosphere was presumably a hot-spot for microbial activity during the root lifetime (Coleman, 1994) the microbial remains near former roots reflect these conditions even in ancient systems.

However, the distribution pattern itself does not allow us to quantitatively estimate the contribution of root-derived OM in rhizoloess samples, because the FA composition did not reveal a consistent trend from R via RL towards L (Fig. 3). This is related to different contributions from plant and microbial origins in these transitions: In the former rhizosphere, the abundance of microorganisms is supposed to be high during the plant's lifetime as they commonly feed on fragments of dead root biomass and the exudates of roots during the lifetime of plants (Coleman, 1994; Jones, 1998). In contrast, the former root tissue (rhizoliths) and sediment (loess) are clearly dominated by plant-derived OM (Fig. 3).

For estimating rhizomicrobial- and root-derived lipids in rhizoloess, quantities of MUFAs and PUFAs were compared for different sample types.

The PUFAs, which are readily degradable because of the number of double bonds (Kawamura et al., 1980), are commonly not regarded in terrestrial sediments like loess, where, e.g. microbial activity and oxygen exposure, might lead to their rapid disappearance. Analogous to lacustrine sediments (Kawamura et al., 1980), the presence or absence, as well as the quantity, of PUFAs in loess are indicators of the incorporation of plant-derived OM on one hand and the level of its degradation and preservation on the other hand. PUFA content normalized to extract yield in L was below detection limit (50 ng g^{-1} C_{org}). The amounts were slightly higher in RL2 (0.009 ± 0.005 mg g^{-1} C_{org}), significantly increased towards RL1 (0.133 ± 0.022 mg g^{-1} C_{org}) and were highest in R (0.191 ± 0.068 mg g^{-1} C_{org}; Fig. 5). This clear differentiation, with two end members (loess and rhizolith) and rhizoloess values in between, was used for the quantification of root-derived input, assuming that R represents the upper limit in the sample set with 100% root-derived OM. L did not contain PUFAs and was therefore used as the other end member with 0% root-derived PUFAs. The root-derived PUFAs in rhizoloess were calculated as follows:

$$\text{portion of root-derived PUFA } [\%] = \left[\sum \text{PUFA}_{\text{Rhizoloess}} \Big/ \left(\sum \text{PUFA}_{\text{Rhizolith}} - \sum \text{PUFA}_{\text{Loess}}\right)\right] \times 100 \quad (5)$$

The portion of root-derived PUFA was lowest in distant rhizoloess (4.9%) and significantly increased in rhizoloess near rhizoliths (69.7%).

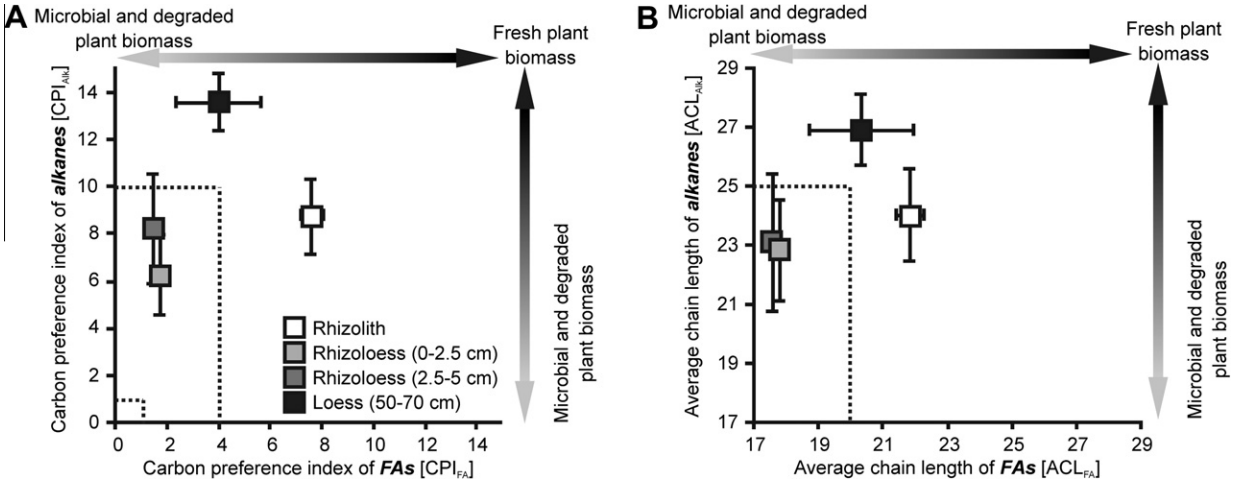

Fig. 4. Comparison of (A) CPI_{Alk} and CPI_{FA} and (B) ACL_{Alk} and ACL_{FA} in rhizoliths, rhizoloess and loess. (A) Dashed lines indicate areas of pure microbial OM (CPI_{Alk} and $CPI_{FA} \approx 1$) and area of strongly degraded OM ($CPI_{Alk} < 10$, $CPI_{FA} < 4$; Cranwell, 1981; Cranwell et al., 1987; Xie et al., 2003; Zhou et al., 2005). (B) Dashed lines indicates area of OM with large microbial contribution ($ACL_{Alk} < 25$, $ACL_{FA} < 20$; Kolattukudy et al., 1976).

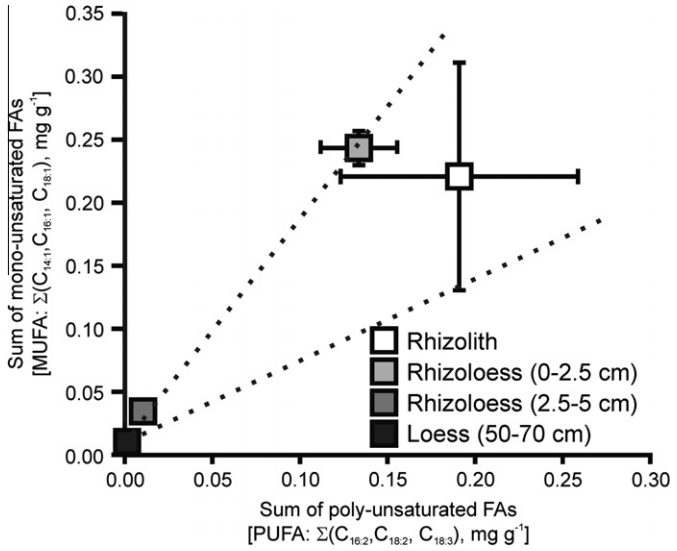

Fig. 5. Abundances of MUFAs and PUFAs in rhizoliths, rhizoloess and loess, normalized to total lipid content (mg g^{-1} extract). Dashed lines represent area of mixing between loess OM and rhizolith OM. Values outside this zone indicate a significant accumulation of additional microbial biomass and degradation products, especially in RL1.

As MUFAs are mainly microorganism-derived (especially some of the $C_{16:1}$ and $C_{18:1}$) but also partly plant-derived (Harwood and Russell, 1984), we use the term "rhizomicrobial-derived MUFA" for both root and associated microbial biomass sources. MUFA content normalized to extract yield was lowest in L and RL2 distant from roots (2.5–5 cm), with 0.010 ± 0.005 mg g^{-1} and 0.034 ± 0.007 mg g^{-1}, and higher in RL1 close to the rhizoliths and in R (0.243 ± 0.013 mg g^{-1} and 0.221 ± 0.090 mg g^{-1}; Fig. 5).

Analogous to PUFAs (Eq. 1) the rhizomicrobial-derived MUFAs in rhizoloess were calculated:

$$\text{portion of rhizomicrobial-derived MUFA } [\%] = \left[\sum \text{MUFA}_{\text{Rhizoloess}} \Big/ \left(\sum \text{MUFA}_{\text{Rhizolith}} - \sum \text{MUFA}_{\text{Loess}}\right)\right] \times 100 \quad (6)$$

According to MUFA, the amount of rhizomicrobial-derived OM accounts for 110.9% in RL1 adjacent to rhizoliths and 11.5% in the distant RL2.

Very low amounts of MUFAs and missing PUFAs in loess clearly show the comparatively severe degradation of loess OM. Consequently, increasing amounts of MUFA and PUFA from L over RL towards R clearly showed the notable contribution of less degraded, potentially younger OM to loess OM in rhizosphere, especially close to roots (Fig. 5). In general, the lower abundances of root-derived PUFAs vs. rhizomicrobial-derived MUFAs can be explained first by a predominantly plant-derived origin of PUFAs and second by an admixture of microorganism-derived remains in MUFAs as well as a stronger degradation of PUFAs in rhizoloess because of the larger number of double bonds. However, both the contribution of root- and microorganism-derived OM in RL1 close to R (70% for PUFA and 111% for MUFA) and the significantly lower contribution in RL2 distant from the rhizoliths (5% and 11%, respectively) may represent minimum values since unsaturated FAs are comparatively susceptible to degradation (Kawamura et al., 1980). The high abundance of MUFAs is most likely related to microorganisms that lived in the former rhizosphere during the lifetime of the roots – similar to the situation in soil (Coleman, 1994), leading to an accumulation of rhizodeposit remains, as well as remains of the microbial biomass which fed on the rhizodeposits. This might explain larger MUFA content in RL1 than in R (Fig. 5).

Assessing the exact contribution of root-derived OM in RL requires examination of other molecular proxies that are less influenced by degradation like, e.g. lignin (e.g. Marschner et al., 2008). In addition, knowledge of the incorporation mechanisms of FAs in the rhizosphere is at present limited (Wiesenberg et al., 2010). Nevertheless, the FA molecular proxies clearly indicate that the post-sedimentary input of root- and rhizomicrobial-derived OM to loess and other terrestrial sediments is an important factor influencing the content and composition of the OM in the sediment.

3.2.2. Alkanes

C_{org}-normalized amount of alkanes was greatest in L and lower in RL and R. The whole sample set was characterized by a typical terrestrial higher plant distribution, with a predominance of long chain odd homologues (C_{25+}; Fig. 6; Eglinton et al., 1962; Kolattukudy et al., 1976). This was confirmed by CPI_{Alk} which was highest in L (13.6 ± 1.0) and lowest in RL1 (6.3 ± 1.9). Values for RL2 and R were intermediate and were similar to each other (8.2 ± 1.1 and 8.8 ± 3.6, respectively), with slightly higher values for R (Fig. 4A).

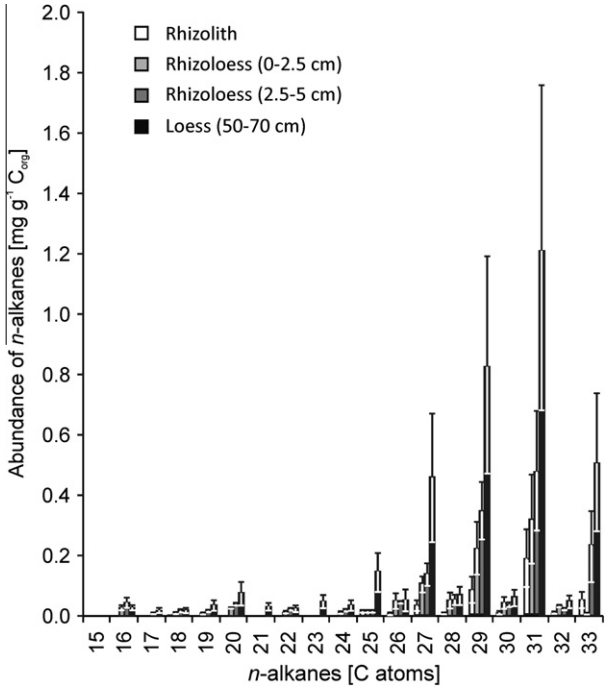

Fig. 6. *n*-Alkane distribution in rhizolith, rhizoloess and reference loess; amounts of alkanes are normalized to C_{org} (mg g^{-1} C_{org}).

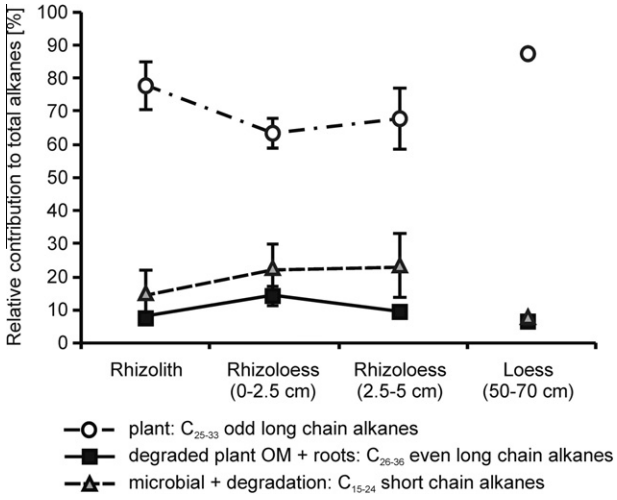

Fig. 7. Relative contribution of alkanes from different origins (microbial and higher plant, as well as degradation products) to total *n*-alkane fraction for rhizoliths and corresponding transects via rhizoloess towards reference loess.

The most abundant *n*-alkanes in R were either C_{29} or C_{31}. In RL the most abundant homologue was the same as in the corresponding R, whereas in loess it was always *n*-C_{31}. In earlier studies, alkane patterns maximizing at *n*-C_{31}, as well as *n*-C_{33}, were attributed to grass vegetation, whereas *n*-C_{29} was not related to a specific vegetation type but could be produced by either grasses or woody vegetation (Maffei, 1996a,b). Within the short chain homologues (C_{15-24}), *n*-C_{16}, *n*-C_{18} or *n*-C_{20} were slightly enriched compared to other homologues, which was especially apparent in rhizoloess. Abundances of all alkanes in RL were intermediate between the corresponding homologues in R and L (Fig. 6).

In R, 77.8 ± 7.2% of the alkanes were contributed by plant-derived, odd long chain homologues (C_{25-33}; Eglinton et al., 1962), while the proportion was lower in RL1 (63.5 ± 4.4%; Fig. 7). At a larger distance from R the relative contribution of these alkanes increased from 68.1 ± 9.2% in RL2 towards 87.5 ± 1.4% in L. The relative abundance of odd long chain alkanes was significantly ($p < 0.05$) different in L, R and RL. The relative amount of even long chain alkanes (C_{26-32}) varied only slightly in the sample set (between 6.6 ± 0.1 in L and 14.3 ± 2.9 RL1). The highest contribution was observed in rhizoloess and decreased in the order RL1 > RL2 > R > L. Similarly, like the even long chain alkanes, the contribution of short chain alkanes (C_{15-24}) was highest in RL samples (22.7 ± 9.6% in RL1 and 22.2 ± 7.2%) and decreased both towards R (14.2 ± 6.9%) and L (5.9 ± 1.5%).

Based on alkane and FA distributions, the OM in the L samples most likely relates to C_3 grass vegetation, whereas rhizoliths were probably formed by woody vegetation like C_3 shrubs or trees. However, determination of the plant species was not possible because of limited knowledge of the lipid composition of root tissue, especially of trees and shrubs.

ACL_{Alk} values in loess (26.9 ± 1.2; Fig. 4B) were comparable to those of higher plant biomass (25–31; Eglinton and Hamilton, 1967). Values were lowest in RL (22.9–23.1), with almost identical values close by (RL1) and distant from rhizoliths (RL2). R was characterized by intermediate values between L and RL (24.1 ± 1.6).

The highest values of ACL_{Alk} and CPI_{Alk} were always obtained for loess, indicating the higher plant origin of the OM (Bray and Evans, 1961; Castillo et al., 1967; Poynter et al., 1989). As demonstrated by FA patterns (Fig. 2), R was also formed by higher plants. However, slightly lower ACL_{Alk} and CPI_{Alk} in R than in L, together with different long chain alkane maximum (Fig. 6) suggest unequal biogenic sources for OM in R and L. Low ACL_{Alk} values in the rhizosphere are most likely attributed to the contribution of microbial remains (Kolattukudy et al., 1976; Harwood and Russell, 1984). In rhizoliths and loess, microbial remains are also present, as shown by $C_{16:0}$ and $C_{18:0}$ FAs (Fig. 2), but this source of OM is masked by the prevalent plant biomass. Low CPI_{Alk} values in RL confirm this and show that even the RL2 distant from R was obviously rooted or received root exudate. This loess was consequently part of the former rhizosphere, where root remains were incorporated and microbial degradation of roots and sedimentary OM took place. This is strongly connected to the hot-spot theory, which hypothesizes greatest microbial activity and hence strongest degradation of OM in soil adjacent to the tips of fine roots (Jones, 1998).

3.3. Implications for rhizolith formation in loess and possible consequences for palaeoenvironmental reconstruction

Molecular proxies showed that rhizoliths in Nussloch derived from vegetation other than loess OM. The latter afforded a combined signal from syn-sedimentary shoot and root biomass with high amounts of long chain FAs (C_{22-32}). This reflects former steppe conditions with grass vegetation (e.g. Wiesenberg and Schwark, 2006), in agreement with loess sedimentation taking place during glacial periods. In contrast, rhizolith OM contained lower amounts of very long chain FAs (C_{26-30}), more likely reflecting roots from shrub or tree vegetation. In general, it is believed that the vegetation cover during loess deposition was minor and consisted mainly of grass (Bai et al., 2009). This suggests that rhizoliths were not formed syn-sedimentary with loess deposition, but roots entered the loess later, followed by calcification during their lifetime (Gocke et al., unpublished results). In many palaeoenvironmental studies based on rhizoliths and other types of pedogenic carbonate in loess–palaeosol sequences, the chronological context of secondary carbonate nodules is not mentioned. Commonly, authors link them to the age of surrounding sediment or soil (e.g. Wang and Follmer, 1998; Wang et al., 2000; Becze-Deák et al., 1997). However, the hypothesis of post-sedimentary rooting of loess was enforced by the Holocene age (3150 yr b.p.) of one rhizolith from

Nussloch (Gocke et al., unpublished results). In contrast, surrounding loess was deposited during the Pleistocene, between 20 and 17 ka (Antoine et al., 2001). The possible existence of such age discrepancies between sediment and calcified roots has only been recognized by a few authors (Pustovoytov and Terhorst, 2004; Cramer and Hawkins, 2009).

Moreover, the above rhizolith sample from Nussloch revealed nearly identical radiocarbon ages for C_{org} and C_{carb} (Gocke et al., unpublished results). This indicates that root calcification took place during plant lifetime and was not a fossilisation process. Lambers et al. (2009) related $CaCO_3$ precipitation adjacent to roots to mass flow induced by the transpirational pull of the living plant. CPI_{FA} and ACL_{FA} values in particular provide further evidence for this theory by showing the relatively low degradation of rhizolith OM (higher values) when compared to loess OM (lower values; Fig. 4A, and B), probably as a result of improved protection of the former root tissue by carbonate encrustation in advance of substantial decay of root biomass.

While deep rooting of loess by grass plants is unlikely because of their root morphology, shrubs and trees are able to penetrate sediments up to 5 m and more (Canadell et al., 1996). It is known for recent soils that living roots can generate huge amounts of exudate and that dead root biomass can lead to a remarkable input of OM (Kuzyakov and Domanski, 2002; Nguyen, 2003). It is therefore likely that, during warmer phases connected with pedogenesis, root-derived OM was also incorporated into parts of the loess deeper than the corresponding soil, and that sediment below this soil could be affected by deeply rooting plants.

Lipid distribution patterns (Figs. 2 and 6) indicate that modification of OM by post-sedimentary processes, including abiotic degradation and microbial decomposition, is strongest in loess and slightly lower in rhizoloess and rhizolith. On the other hand, the abundance of microbial remains was higher in RL than L, as indicated by CPI_{Alk}, ACL_{Alk} and the presence of unsaturated FAs in RL. This supports the idea of stronger degradation of plant remains by microbial reworking in the former rhizosphere, leaving relatively larger portions of microbial remains therein. Based on PUFAs, the minimum contribution of root-derived OM to loess OM of 69.7% was calculated for RL at a distance of 0–2.5 cm to R. A notable post-sedimentary contribution of root-derived OM at greater distances from rhizoliths is likely and should be estimated in future studies. Particularly for terrestrial sediments, which are often poor in C_{org}, post-sedimentary input of OM might lead to a remarkable overprint of the composition of the original (i.e. syn-sedimentary) OM. In rhizoloess no visible remains of roots and no obvious colour change vs. the surrounding sedimentary material were observed, suggesting that the post-sedimentary contribution of root-derived OM might have been underestimated in previous studies. This could explain some uncertainties in bulk C_{org} radiocarbon (^{14}C) ages and $\delta^{13}C_{org}$ measurements in loess–palaeosol sequences (Hatté et al., 1999; Rousseau et al., 2007). It was assumed previously that $\delta^{13}C_{org}$ values might represent mixed signals from syn-sedimentary prevailing vegetation and additional sources. This additional OM was thought to be either inherited from the source material of loess (Liu et al., 2007) or incorporated from percolating soil solutions of modern soil (Zhou et al., 1997). Post-sedimentary penetrating roots themselves, however, were never discussed as a possible origin. This preliminary study is the first to demonstrate considerable post-sedimentary contribution of root-derived OM to terrestrial sediments. For the first time, an attempt was made to quantify this overprint using organic geochemical analysis. Further investigations, and from other sites, are necessary to elucidate the impact of post-sedimentary incorporated OM in loess–palaeosol sequences as well as the environmental conditions which lead to formation of rhizoliths and related rhizodeposits.

4. Conclusions

For the loess–palaeosol sequence at Nussloch, SW Germany, we have shown that the remains of OM in rhizoliths are suitable for elucidating their formation and influence on the surrounding sediment. Comparison of FA and alkane distributions in loess and rhizoliths suggested grass biomass as the source for loess OM, in agreement with loess deposition during glacials, with scarce vegetation cover. Root biomass of shrubs or trees was found to be the origin of the rhizoliths. This, together with radiocarbon data from the same section, disproves the prevalent opinion about rhizolith formation taking place simultaneously with loess sedimentation. While loess sedimentation occurs under steppe-like conditions, roots entered the loess later, probably under different climatic conditions, and consequently derive from different vegetation.

Lipid analysis combining several FA and alkane proxies, including CPI and ACL, revealed information regarding the contribution of post-sedimentary incorporated plant biomass and the intensity of degradation of plant-derived biomass. Based on PUFAs, we quantified the amounts of root-derived OM incorporated into loess adjacent to rhizoliths by comparison with reference loess from the same depth, which accounted for at least 70% of the OM adjacent to rhizoliths. Furthermore, MUFAs argued for an enrichment of root-derived and associated microbial biomass remains in the vicinity of rhizoliths. ACL and CPI molecular proxies showed that the influence of the former roots by generation of rhizodeposits led to a modification of the OM composition in the rhizosphere, which was notable at least to a distance of 5 cm from the rhizolith. The consequential overprint of syn-sedimentary incorporated loess OM by younger biomass from other sources might entail uncertainties regarding chronological (^{14}C) and palaeoenvironmental ($\delta^{13}C$) studies. Therefore, more research is required to elucidate the influence of larger deeply rooting plants on the composition of OM in the underlying sediment.

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