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Black carbon: Fire fingerprints in Pleistocene loess–palaeosol archives in Germany

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A B S T R A C T

Past environmental changes were frequently accompanied by changes in fire regimes. However, the extent to which the residue of ancient fires (black carbon, BC) is abundant in Pleistocene palaeosols remains largely unknown, and whether, and to which degree its occurrence and composition relates to pedogenetic processes and palaeoenvironmental change. We studied three Pleistocene loess–palaeosol sequences from western Germany for systematic variation in BC quantity and quality during Marine Isotope Stages 5e to 4 (ca. 130–65 ka BP), using the benzene polycarboxylic acid (BPCA) oxidation method. Palaeopedogenetic processes were elucidated from grain size distribution, colour, organic and inorganic carbon and Ba/Sr ratio. The results showed that BC peaked during phases of soil formation, indicated by increases in Ba/Sr, carbonate loss and colour change. Its concentration reached 0.6–2.1 g BC C/kg of former topsoil. The content was close to the detection limit in the parent loess and subsoil, suggesting that there was little if any vertical translocation. Parameters for BC quality (i.e. proportion of mellitic acid) were typical for BC derived from the burning of grass and leaves, as common for tundra-like and forest steppe vegetation dominating in stadials and interstadials of the Weichselian Glaciation. We conclude that BC was preserved in, and bears comparable information in, the three palaeosols. Hence, we recommend BPCA analysis of terrestrial archives for regional fire regime assessment in the Pleistocene.
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1. Introduction

During the Pleistocene, the Northern Hemisphere was subject to major climate changes between cold glacial and warm interstadial/interglacial periods, causing profound ecosystem change and change in the frequency and intensity of natural fire regimes (Wang et al., 2005, 2012; Daniau et al., 2010). The fire input provides information, at least in part, on past vegetation change, because different ecosystems recover differently from a fire event. While grassland, for instance, recovers quickly and has thus been prone to frequent burning, other ecosystems, like those inhabited by deciduous trees, usually burn less often (Pyne et al., 1996; Dube, 2009; Thonicke et al., 2010). Moreover, grass and the leaves of trees usually burn at low temperature, whereas human-induced fires (domestic or clearing activity) are usually accompanied by higher burning temperatures (Cohen-Ofri et al., 2006; Braadbaart and Poole, 2008; Maggetti et al., 2011). Hence, reconstructing fire regimes may be a useful tool for elucidating past changes in climate and human-environment interactions (Davis, 1965; Wang et al., 2005; Marlon et al., 2008, 2013; Tan et al., 2011).

Abundant information is available on the occurrence of fire residues (black carbon, BC) in marine and limnic sediment cores (Marlon et al., 2013). Yet, even more BC remains in the terrestrial environment and has been discovered in many terrestrial archives, such as loess–palaeosol sequences (Daniau et al., 2010; Tan et al., 2011; Wang et al., 2012). These archives are, however, usually well aerated. It is known that BC may be prone to aerobic degradation (Hamer et al., 2004; Knoblauch et al., 2011), reducing its preservation in such archives during the Late Quaternary. On the other hand, it may be argued that, with a lack of C sources, microbial activity would be usually low (Schnürer et al., 1985) if at all detectable in deep palaeosols, thereby allowing the remaining BC to be preserved once buried below the topsoil, as reported for example, for labile organic matter (OM) in subsoils (Lützow et al., 2006). Moreover, BC contains recalcitrant aromatic structures (Keiluweit et al., 2010), which are among the most stable components of soil OM (SOM; Brodowski et al., 2006; Czimczik and Masiello, 2007)

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and has been discovered in soils and sediments up to several thousands and millions of years in age (e.g. Masiello and Druffel, 1998; Scott, 2000; Antal and Grønli, 2003; Grasby et al., 2011). Also, within a 100 yr combustion chronosequence, Schneider et al. (2011) did not observe any change in the amount and quality of BC in soil, possibly because, once it is incorporated into soil, it may be protected from decay by occlusion within soil aggregates (Brodowski et al., 2006; Liang et al., 2008). To elucidate the degree to which the signal from BC is preserved in palaeosols, it would be helpful to relate changes in BC quantity and quality to other, already deciphered palaeoenvironmental changes, in such terrestrial archives.

In Europe, the climate in the younger Pleistocene was prone to significant changes in temperature, moisture and vegetation (Smalley, 1997). This led to frequent changes in loess deposition during cold phases and soil formation during warm phases (Smalley, 1995, 1997) and likely also to more and less favourable conditions for vegetation fires. In Central Europe, the invasion of vegetation at the beginning of the interglacials and interstadials started with tundra-like vegetation, and birch and pine-birch woodlands (Menke and Tynni, 1984) and, depending on temperature and moisture, led to the formation of thermophilous deciduous woodlands with pine and mixed oak forest in the Eemian interglacial (Caspers et al., 2002). During transitions from colder to warmer phases in the Lower Weichselian stadials and interstadials, the frequency of fires increased (Daniau et al., 2010). Hence, it is likely that changing ecosystem properties would be reflected in the Late Pleistocene BC record.

Promising records of BC have been found in Chinese Pleistocene to Holocene loess–palaeosol sequences, which could be linked to climate change (Wang et al., 2005, 2012; Tan et al., 2011). Similar approaches for Pleistocene fire residues in Central European loess sequences are, to our knowledge, lacking. To detect BC in such sequences, it may be possible to trace soil luminance or lightness (Schulze et al., 1993; Konen et al., 2003), which are affected by the accumulation of BC (Spielvogel et al., 2004; Eckmeier et al., 2010). In particular, the degree of blackness of a soil may serve as an indication for enhanced input of fire residue (Schmidt et al., 1999, 2002; Eckmeier et al., 2010). The concentration and quality of soil BC can be estimated from chemothermal oxidation of fire residues to benzene polycarboxylic acids ("BPCA method", Glaser et al., 1998; Brodowski et al., 2005). The relative proportion of products with 5–6 carboxyl groups was shown to be sensitive to fire temperature (Schneider et al., 2010, 2013; Wolf et al., 2013), thereby allowing differentiation of fire regimes, i.e. grass and forest groundfire, shrubland burning and anthropogenic high temperature wood fires (Wolf et al., 2013).

The objective of this study was to see whether or not we could detect BC in palaeosols and whether its signature in terms of BPCA composition would correspond to the assumed burning temperature of the prevailing ecosystems in the Eemian (ca. 115–128 ka) and the Early Weichselian (ca. 65–115 ka BP). In addition, we aimed at elucidating the prevalent fire regimes during the 70,000 yr in question. For this purpose, we sampled three loess–palaeosol sequences of late Pleistocene age (Marine Isotope Stages MIS 5 to MIS 4) from the Elsbach Valley (lower Rhine Embayment), Koblenz–Metternich (Moselle River Valley) and the Tönchesberg (East Eifel Volcanic Field) and analysed these sequences using the BPCA method. We hypothesised that we would find BC accumulation in all the palaeosols, but with variation related to different soil formation phases. In addition, we assumed that it would be possible to recognise simultaneous maxima in BC quantity in the three sequences, i.e. as being representative for the regional burning conditions. Data were supported by analysis of the grain size distribution and the elemental composition of loess and palaeosols. These parameters are often used to discriminate unconformities in loess–palaeosol sequences and to identify material provenance (Folk and Ward, 1957; Friedman, 1979; Bui et al., 1989; Blott and Pye, 2001) and soil formation processes (Birkeland, 1999; Hill, 2005; Bokhorst et al., 2009; Buggle et al., 2011).

2. Material and methods

2.1. Loess–palaeosol sequences

The sequences are from the middle terraces of the rivers Moselle and Rhine in western Germany, including the section at Koblenz–Metternich (50°21′N, 7°33′E), the section at Tönchesberg in an intra-crater depression of the East Eifel Volcanic Field (50°22′N, 7°21′E) and a section in the Elsbach Valley (51°02′N, 6°29′E) in the Lower Rhine Embayment. All sequences included numerically dated loess horizons, as well as buried topsoil (Ah horizon) that developed during the Lower Weichselian interstadial phases (Boenigk and Frechen, 2001; Fischer et al., 2012).

The loess and loess derivatives were deposited during the penultimate (Saalian) and last glaciation (Weichselian) on gravel of the fluvial terraces of Lower and Middle Pleistocene age (for the Koblenz–Metternich and Elsbach Valley sequences see Boenigk and Frechen, 2001) or on volcanic material (MIS 7 to MIS 2, Tönchesberg sequence; Frechen, 1994; Schmidt et al., 2011). In the loess deposits, soil horizons are intercalated, and were slightly reworked on the slopes of the river valleys before the next phase of loess sedimentation (Boenigk, 1990; Boenigk and Hagedorn, 1996).

2.2. Genesis of sequences and soils

2.2.1. Koblenz–Metternich (Moselle River Valley)

The Koblenz–Metternich loess–palaeosol sequence is in the valley of the River Moselle, close to the opening to the Middle Rhine Valley at the city of Koblenz. Several studies have described the palaeosols as a sequence of brown forest soils and a chernozem as the "upper-pedocomplex" of mainly Lower Weichselian age (MIS 5a–d; sequence no. A, B1 from Boenigk et al., 1994; Boenigk and Frechen, 1999; Hill, 2005).

The sediment series consists of carbonate-enriched, reworked loess derivatives (from the penultimate Saale Glaciation, MIS 6) at the bottom of the so-called upper pedocomplex (Fig. 1). The deposition of the reworked loess derivatives was dated to a minimum age of 92–116 ka and 77–92 ka (Late Eemian to Lower Weichselian) from thermo- and infrared-stimulated luminescence, respectively (TL and IRSL ages; corresponding to MIS 5d; Boenigk and Frechen, 2001). However, a fading correction, as suggested recently for luminescence dating (Wacha and Frechen, 2011), was not applied, so that slight age underestimation is possible for the Koblenz–Metternich profile. The overlying reddish brown clay accumulation horizon (Bt; Fig. 1) was attributed to advanced soil development during the Lower Weichselian Brørup Interstadial (corresponding to MIS 5c; Boenigk and Frechen, 2001). A leached topsoil horizon (E), also associated with MIS 5c, follows (Boenigk and Frechen, 2001). On top of this, a sequence of dark, slightly reworked topsoil sediment (Ah horizon; Fig. 1) was found. This complex is overlain by the "marker loess", a chronostratigraphic detail commonly found in the region and dated to the transition phase of the Lower to the Middle Weichselian (corresponding to MIS 5–4; TL dated to ca. 67 ka; Hill, 2005). On top of the marker loess, dark coloured humic rich soil sediments and a series of partially reworked light coloured loess layers followed, with a substrate TL age of 75–77 ka and an IRSL age of 62–67 ka, respectively (corresponding to the Middle Weichselian; MIS 4; Boenigk and Frechen, 2001).

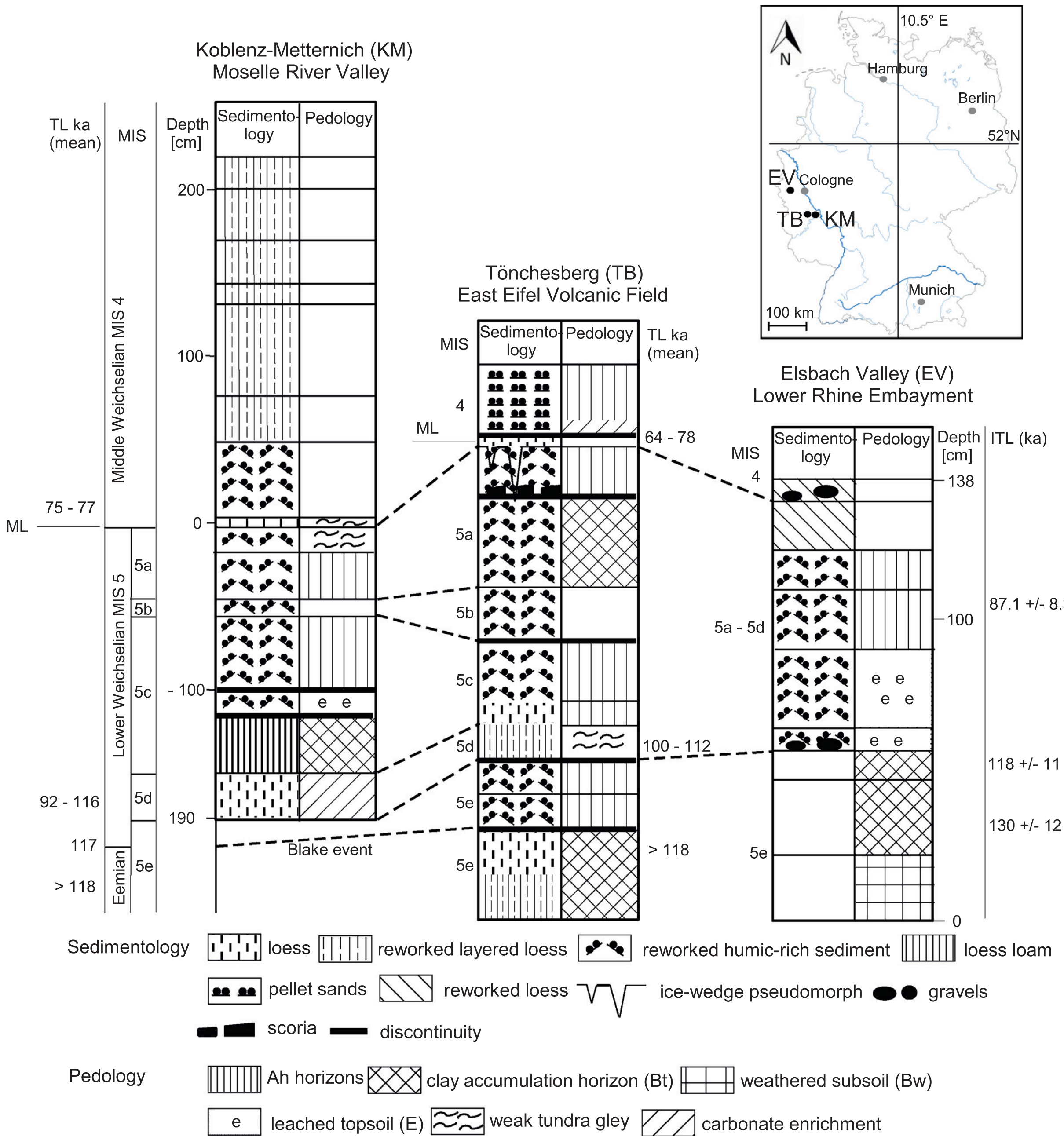

Fig. 1. Sedimentological and pedological scheme. Sequence sketches are simplified from Boenigk et al. (1994, sequence A, Koblenz–Metternich), Boenigk and Frechen (2001, Tönchesberg sequence, sampled from different depths in a quarry) and Fischer et al. (2012, Elsbach Valley sequence) (TL, ITL, thermo- and infrared stimulated luminescence ages; ML, marker loess, depth zero in profile KM; map of Germany was modified from http://d-maps.com).

2.2.2. Tönchesberg (East Eifel Volcanic Field)

To study the effects of differing substrate and climate on BC deposition, an Eemian palaeosol remnant (clay accumulation horizon; Bt) and a Weichselian topsoil (A horizon) were sampled at a loess–palaeosol sequence in the Tönchesberg scoria cone, situated in the East Eifel Volcanic Field (Boenigk and Frechen, 2001). Two samples were taken from the Eemian clay accumulation horizon (Bt), which was dated to a substrate TL age of > 118 ka (MIS 5e; Boenigk and Frechen, 2001; Schmidt et al., 2011). One sample was collected from a reworked topsoil (a horizon). It formed in a moist environment related to MIS 5c (Brørup; TL and OSL age range between 100 and 115 ka, depending on dating technique; Boenigk and Frechen, 2001; Schmidt et al., 2011). Above this, a horizon of reworked humic-rich soil sediment with clay accumulation characteristics (BtAh) was correlated with MIS 5a (Odderade). The marker loess was deposited on top and was dated to the Middle Weichselian (MIS 4). The TL, IRSL and OSL ages range from 64–78 ka, with 71 ka being the most appropriate estimate (Fig. 1; Boenigk and Frechen, 2001; Schmidt et al., 2011). At the top of the palaeosol sequence, a topsoil (Ah) horizon was found, which formed on sand size pellets of decalcified loess.

2.2.3. Elsbach Valley (Lower Rhine Valley)

The Elsbach Valley sequence (archaeological documentation number FR 2006/0086, feature 5) is from the northeastern part of the Lower Rhine Embayment, the Garzweiler brown coal open cast mining area. At the base of the sequence – with a thickness of 2.7 m in total – a series of weathered (Bw) and clay accumulation subsoil horizons (Bt) was found (Fischer et al., 2012). The lower part, including the weathered subsoil, was dated from isothermal TL (ITL) to a burial age of 130 ± 12 ka (Fig. 1), which implies that soil formation likely occurred during the Eemian interglacial (MIS 5e; Fischer et al., 2012). The upper part of the series, including the clay accumulation horizons, was dated to a substrate age of 118 ± 11 ka (MIS 5e; Fischer et al., 2012). Separated by reworked loess containing fine gravel, two leached topsoils (E horizons) followed (Fig. 1). Overlying humic layers (Ah horizon) exhibited an ITL substrate age of 87.1 ± 8.3 ka and were hence attributed to the Lower Weichselian interstadial phases (MIS 5a–d). On top of the sequence, reworked loess sediments of the early Middle Weichselian (MIS 4) were found (Fig. 1).

2.3. Methods

2.3.1. Grain size

For the samples from the sequence at Koblenz–Metternich (Moselle River) and that at Tönchesberg (the volcano) the 63–0.63 μm fraction was analysed with a Sedigraph (Micromeritics 5100, Mönchengladbach, Germany). Before analysis, OM (boiling with H_2O_2) and carbonate (33% HCl) were removed from bulk samples (10 g). Samples were then dispersed in 12.5 ml 0.1 M $Na_4P_2O_7$ overnight and the sand fraction separated from clay and silt by sieving to < 63 μm. Samples of the Elsbach Valley were analysed with a Laserbeuger 0.04–2000 μm instrument (Beckmann Coulter LS13320, Fullerton, California). We used a grain size ratio [(cSi + fS)/(mS + cS)] which excluded the clay fraction and, hence, bias from analytical differences between the two methods applied. The ratio unravels changes in silt deposition relative to sand, which are commonly related to different phases of loess sedimentation (Schlichting et al., 1995). Grain sizes used for calculating the ratio were coarse silt (cSi, 20–63 μm), fine sand (fS, 63–200 μm), medium sand (mS, 200–630 μm) and coarse sand (cS, 630–2 mm).

2.3.2. Colour

Colour was measured for dry and homogenised sediment samples using a spectrophotometer (Konica Minolta CM-5). The colour spectra were obtained in the 360–740 nm range and converted to the CIELAB Colour Space ($L^*a^*b^*$, CIE 1976). The $L^*a^*b^*$ values indicate the extinction of light, or luminance, on a scale from L^* 0 (absolute black) to L^* 100 (absolute white), and express colour as chromacity coordinates on green ($-a^*$) to red ($+a^*$) and blue ($-b^*$) to yellow ($+b^*$) scales.

2.3.3. Organic carbon (C_{org}) and carbonate

Total C content was determined with a Fisons NA 2000 elemental analyzer. The method involved dry combustion to CO_2 and its quantification using a heat conduction detector. Carbonate was removed with 15% HCl overnight (> 12 h). Samples were added to a glass fibre filter (GF 6), and vessel and filter were rinsed with deionized water until neutral. Filters were dried in an oven for 2 h at 30–40 °C before C_{org} and N analysis. Carbonate content was calculated from $(C_{total} - C_{org}) \times 8.333 \times 10$.

2.3.4. X-ray fluorescence (XRF) measurements

Bulk samples were sieved to < 63 μm and wax pressed. Elemental analysis was conducted with an XRF device (SPECTRO XEPOS, SPECTRO Analytical Instruments, Germany). Among the 50 elements analysed, Ba/Sr was used to discuss soil formation processes. The preferential loss of the geochemically mobile element Sr vs. the comparatively immobile Ba is related to carbonate dissolution and leaching (Bokhorst et al., 2009).

2.3.5. Assessment of BC content and quality from oxidation to BPCAs

The BPCA method (Glaser et al., 1998) is suitable for quantifying BC in environmental samples and obtaining information on its composition (degree of polyaromatic condensation) from the relative proportion of mellitic acid (B6CA) (e.g. Hammes et al., 2008a; Roth et al., 2012; Wolf et al., 2013). In brief, 500 mg milled sample were hydrolysed with 4 M CF_3CO_2H to remove polyvalent cations following the protocol of Brodowski et al. (2005). After digestion with HNO_3 at 170 °C and addition of internal standards, samples were cleaned up, derivatised and measured using gas chromatography coupled with flame ionization detection (GC-FID; Agilent 6890; Optima-5 column, 30 m × 0.25 mm i.d., 0.25 μm film thickness; Supelco, Steinheim, Germany). For BC concentration, BPCA yield was corrected with a conversion factor of 2.27 established by Glaser et al. (1998) as representing a conservative estimate (Brodowski et al., 2005). The qualitative interpretation of BC is based on the ratio of five to six times carboxylated acids (B5CA/B6CA; Wolf et al., 2013).

2.4. Statistical analysis

Data were tested for significant differences using SIGMAPLOT 11.0. One Way Anova was used if parameters passed Normality-Test (Shapiro–Wilk); if the test failed, Anova on Ranks were calculated employing a Kruskal–Wallis-H Test (comparison of groups) or a Mann–Whitney Rank Sum Test (comparison of two groups).

3. Results

3.1. Proxies for parent material

Different sources of loess are indicated by changes in grain size. Here, grain size distribution varied between samples in one loess–palaeosol sequence and between the three sequences: the (cSi + fS)/(mS + cS) ratio was highest for the soil remnants correlated with MIS 5d and early to middle MIS 5c of the Koblenz–Metternich sequence, as well as for samples associated with MIS 4, with values increasing up to 39.4. In contrast, the topsoil horizons attributed to MIS 5a–5c exhibited a lower ratio of 6.9–11.1 (Fig. 2a). In the Tönchesberg and the Elsbach Valley sequence, the grain size distribution was stable around 5 ± 2 and 6 ± 1, respectively.

3.2. Proxies related to soil formation

Soil forming processes are indicated by changes in OM content (humus formation in topsoil horizons), decalcification (a prerequisite for the reformation and illuviation of clay minerals), as well as by changes in Ba/Sr (a quantitative indicator of carbonate dissolution and leaching within a given loess deposit).

Humus formation was evident from elevated C_{org} content at MIS 5a (warm period) and MIS 5b (cool period), exceeding 5 g/kg in the former topsoils (Fig. 3). The highest concentration of 8.2 g/kg C_{org} was in the topsoils of Koblenz–Metternich and the Tönchesberg sequence, correlating with MIS 5a and MIS 5c, respectively. The C_{org} content of the other soil horizons, as well as of the loess derivatives and reworked loess deposits was significantly lower, ranging from not detectable to 2.7 g/kg in subsoil (Bt) horizons correlating with MIS 5 (Fig. 3a).

In all three loess–palaeosol sequences, carbonate was present in sediments attributed to MIS 4 (25–210 g/kg), as well as in the MIS 5d sediments at Koblenz–Metternich and Tönchesberg (MIS 5a, e; Fig. 2).

Once loess has been decalcified, it is prone to enhanced weathering and transformation and translocation of, for example,

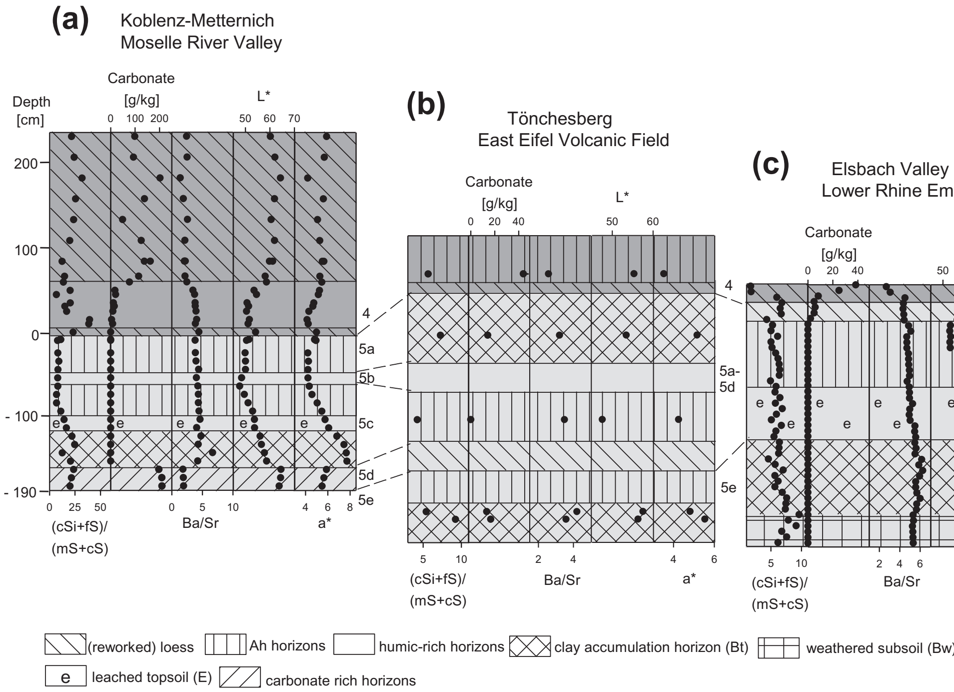

Fig. 2. Grain size index, carbonate concentration and Ba/Sr ratio and colour (lightness (L^*) and chromacity (a^*)) as indicators of changes in sediment provenance and soil formation. A change in loess provenance is likely between MIS 5 and MIS 4 in the Koblenz–Metternich (a) and the Elsbach Valley (c) sequence, but was not noticed at Tönchesberg (b). The content of carbonate, Ba/Sr and colour reveal good discrimination of the reworked loess deposits, in contrast to the palaeosols and humic-rich layers of early MIS 4 (dark grey) and MIS 5 (light grey).

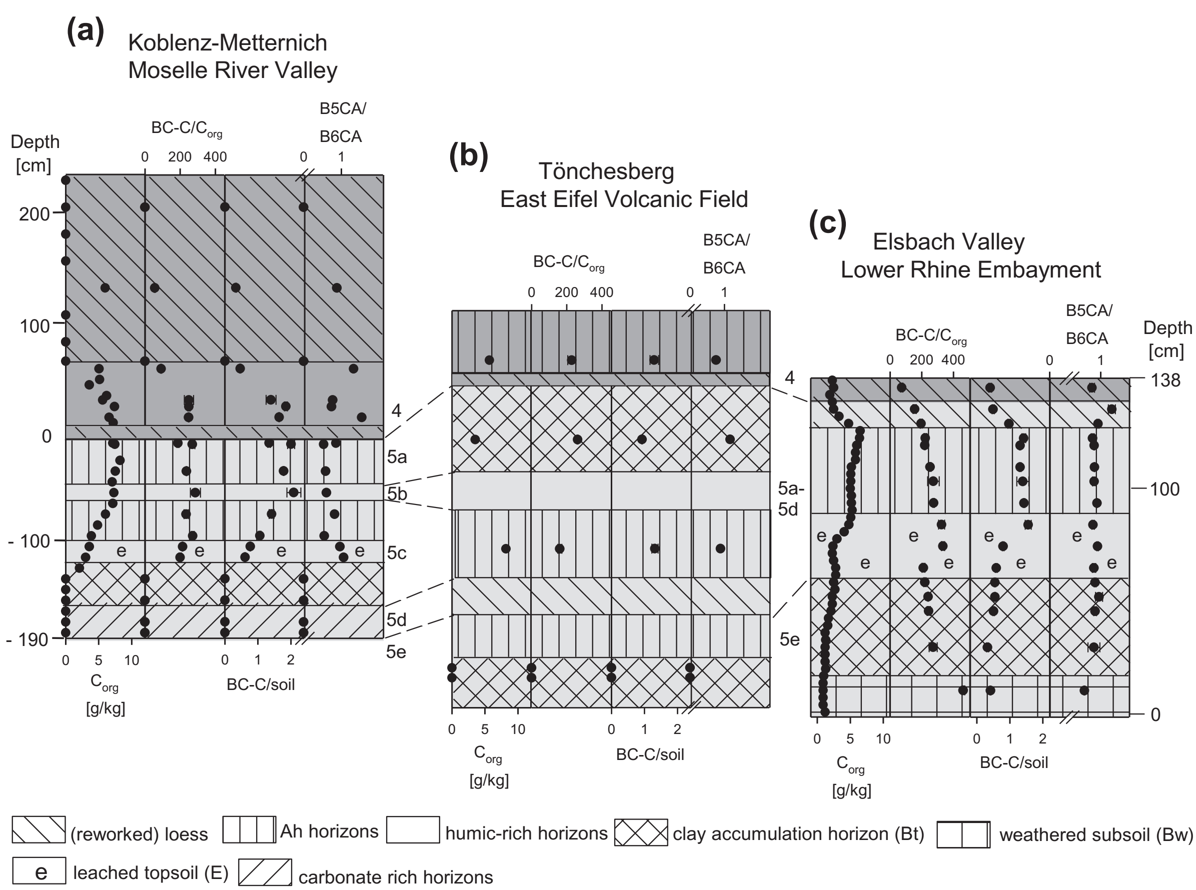

Fig. 3. Organic carbon and BC were detected in the humic rich and Ah horizons of the early MIS 4 (dark grey) and MIS 5a–5d (light grey). Within the given time slices BC amount was similar at all sequences. Variability in relative BC content and quality was low throughout the MIS 5 interstadial phases.

minerals, resulting in clay illuviation. For all samples from reworked loess layers and loess derivatives Ba/Sr values were < 4 and increased to > 4 in the soil horizons of the Koblenz–Metternich and Elsbach Valley sequences. Accordingly, the maximum Ba/Sr values were detected in the clay-enriched subsoils at Koblenz–Metternich (MIS 5c) and at Elsbach Valley and Tönchesberg (MIS 5e; Fig. 2) due to intense soil formation. In the Eemian Bt horizon of Tönchesberg (MIS5e), carbonates indicate a secondary carbonate precipitation (Fig. 2b).

3.3. Colour measurements

The luminance parameter L^* was < 55 in the OM-enriched ancient topsoil horizons from all loess sequences (Fig. 3; r^2 0.71, $p < 0.0001$). In the Elsbach Valley sequence, the dark colour of the upper Ah horizon also clearly separated it from the underlying rust-spotted and leached topsoils (E horizon). The darkest colour (lowest L^* values of 48) was in the upper part of the MIS 5c and the MIS 5b horizon of the Koblenz–Metternich sequence and the Tönchesberg sequence.

The reworked loess deposits and loess derivatives of the Koblenz–Metternich sequence were characterised by lighter L^* values around 60. The Eemian weathered subsoil (Bw) and the clay accumulation horizons (Bt) in the Elsbach Valley sequence reached a maximum of L^* around 66.

The redness values were comparable for all non-pedogenetically influenced loess deposits (a^* 5.5–6) for all three sequences. The highest values, i.e. most reddish colour were measured for the subsoil (Bt and Bw horizons; Fig. 2) which could be related to the advanced stage of soil formation (see also Ba/Sr), via brunification or hydromorphological processes or both (Barron and Torrent, 1986; Viscarra Rossel et al., 2006; Fig. 2).

3.4. BC proxies: the BPCA method

The BC concentration exceeded 1 g BC C/kg in all topsoil and humic-rich horizons of the loess–palaeosol sequences (Fig. 3). The highest amount (2 g BC C/kg) was found in the transition from phase MIS 5c to MIS 5b in the Koblenz–Metternich sequence. This is in line with findings from the Ah–Bt horizon correlating with MIS 5a from the Tönchesberg sequence (0.93 g BC C/kg) and the Ah horizons found at Elsbach Valley (1.5 g BC C/kg). The accumulation was not restricted to the surface soil horizons and the subsoils contained BC (0.3–0.98 g BC C/kg), though not in all cases [i.e. the Eemian clay accumulation horizon (Bt) of the Tönchesberg sequence did not contain any BC]. Overall, total BC accumulation correlated with the accumulation of C_{org} (r^2 0.72, p 0.02 for Koblenz–Metternich and 0.86, p 0.36 for Elsbach Valley).

The BC quantities detected in the soil remnants of the three sequences were of similar magnitude (p 0.71). Hence, all sites received similar BC input despite their specific local properties (e.g. substrate, position). However, among the soil and humic-rich horizons, the BC content differed significantly, as indicated above ($p \leqslant 0.001$; Fig. 3).

Loess deposited during stadial phases of the Last Glacial was largely devoid of BC. In the reworked loess layers of the Koblenz–Metternich sequence, no BC was detectable, with one exception (Fig. 3a). Also in the Elsbach Valley, BC content of the reworked loess was small. This is in line with the lack of vegetation during these times (Grüger, 1989).

The ratio of carboxylated combustion markers – B5CA/B6CA – enables reconstruction of the intensity of the thermal impact on charcoal (Wolf et al., 2013). Here, B5CA/B6CA values ranged from 0.79 to 0.95 in the topsoil horizons (Fig. 3a and b) of Koblenz–Metternich and Tönchesberg. For the Elsbach Valley the ratio had values < 0.95 for the topsoil horizons. Elevated values were found for the humic-rich loess layers of early MIS 4 and the leached topsoil (E horizon) related to middle MIS 5c for Koblenz–Metternich, as well as for the sample from the topsoil horizon with clay accumulation characteristics (BtAh; MIS 5a; Tönchesberg). Minimum average values were found at Elsbach Valley, with 0.71 as the lowest value for the intensively weathered subsoil related to the last interglacial (MIS 5e), and one outstanding high value of 1.2 for the topmost sample related to MIS 5a stage (Fig. 3c). Hence, BC quality changed in all the loess–palaeosol sequences. However, in contrast to the absolute BC content, the B5CA/B6CA was not consistent for a given time slice among all the sites. Whether or not these changes were related to changes in fire regime or due to soil formation processes is discussed below.

4. Discussion

In order to use the BC amount and quality, the BPCA pattern, as an indicator for past fires within these loess–palaeosol sequences, its stability was first evaluated. The degree to which BC is refractory is in dispute (Czimczik and Masiello, 2007). The literature is rich in studies showing that BC is vulnerable to degradation by microorganisms (Baldock and Smernik, 2002; Hockaday et al., 2006). Hammes et al. (2008b) found that BC was degraded by ca. 25% over a century. In contrast, Schneider et al. (2011) did not observe any hint of BC degradation in a 100 yr soil chronosequence. Here, we found a median BC concentration of 238.6 g BC C/kg C_{org} in all palaeo-topsoil horizons. This correlates with BC amount in recent soils (Schmidt et al., 2001; Glaser and Amelung, 2003; Dai et al., 2005; Rodionov et al., 2010). Even if parts of this BC were selectively enriched during the decomposition of non-pyrogenic OM and less-severely charred components, a significant proportion was still preserved in the palaeosols.

Correlation between BC, C_{org} and colour was observed in all sections. Likely, C_{org} content reflects ancient OM input: the topsoil horizons, i.e. the former land surface, were most prone to biomass accumulation and thus also to burnt biomass (BC). Elevated BC concentration again correlated with blackness (r^2 0.83 for Koblenz–Metternich sequence, 0.66 for Elsbach Valley, $p < 0.0001$ for both; Fig. 3a). However, the correlation of colour with C_{org} was better and also depended on soil formation and erosion (see Section 3.3); hence, we refrain from further use of colour as an indicator for BC.

Apart from BC content, interpreting the BPCA pattern and amount of mellitic acid from charcoal was suggested as a "molecular thermometer" for combustion conditions (Schneider et al., 2010, 2013; Wolf et al., 2013). These studies found an offset to mellitic acid between lab-produced charcoal and natural charcoal, likely pointing to a higher contribution from condensed BC to the natural environment. This might be explained by the sampling strategy in the lab, which depicts charcoal alone and excludes condensation products from the gas phase (hence, minimising the proportion of mellitic acid). Here, we also did not have pure charcoal but a mixture of the BC continuum within soil and SOM, with uncertainty about the degree to which there had been changes in BC quality upon alteration. However, the B5CA/B6CA values were all in the range 0.75–0.95 for the topsoil horizons. According to Wolf et al. (2013), such a signature is typical for natural charcoal from grass fires, with values ranging from 0.8 to 1.4. This is in agreement with the prevalent tundra-like vegetation during the stadials of MIS 5 (see also Section 4.2).

4.1. Potential factors influencing BC record

BC in loess–palaeosol sequences may be inherited in part from soils formed in the loess source regions. Indeed, the loess provenance was different for the three sites, and between the different periods of loess deposition at Koblenz–Metternich (as indicated by grain size differences, Fig. 2). The morphological position of the Koblenz–Metternich sequence, in between the EW-striking Moselle and the NS-striking Rhine Valley, allowed input of different aeolian sediments, leading to the grain-size change between soil sediments related to MIS 4 and MIS 5 (Fig. 2a). Boenigk et al. (1994) related higher sand concentration above the marker loess to an elevated contribution of aeolian sediments from the Moselle Valley. However, during all periods, the main source of loess was the floodplain of the River Rhine (Boenigk et al., 1994) and differences in loess provenance among sites were only small. However, if BC also stemmed from aeolian transport, i.e. was deposited with the loess, we might find correlation of grain size with BC content and BPCA distribution, which was, however, not the case.

The soil which formed on the loess substrates after deposition did not show any significant change in BC quality and quantity among sites (Fig. 3a). Likewise the BC in all three palaeosol sequences stemmed from the same type of fire – i.e. investigating BC in terrestrial archives seems to provide a representative view of regional BC input. In pure loess, BC was low or not detectable. Hence, we conclude that all BC found in the palaeosol horizons was produced and deposited during periods of soil formation.

The degree of soil formation in the presence of carbonaceous loess as substrate is first of all reflected in a loss of carbonate. During warm and moist interstadial phases like those of MIS 5 the removal of the readily soluble elements Ca and Mg are indicators for initial weathering (Nesbitt et al., 1980). Accordingly, we found all topsoil and subsoil horizons depleted in, or free from, carbonate (Fig. 2). The unweathered Last Glacial loess at the studied sequences from the Middle and Lower Rhineland often contains ca. 10–20% primary carbonate (Blume et al., 2002), which was partly or completely leached during soil formation. The fluctuation in carbonate content and in Ba/Sr at the three loess–palaeosol sequences indicates that different soil forming processes, like decalcification and leaching, as well as secondary carbonate enrichment, took place after deposition of the loess and during soil formation (Fig. 2; Boenigk et al., 1994; Hill, 2005). A more uniform Ba/Sr ratio in the Elsbach Valley sequence (Fig. 2c) was related to secondary, post-pedogenetic input from lateral subsurface flow, which likely appeared after soil formation on top of the clay-enriched, water-impermeable subsoil correlating with MIS 5e (Bt; Fischer et al., 2012). However, the C_{org} and BC contents were below detection limit in the palaeo-subsoils of Tönchesberg and Koblenz–Metternich (Fig. 3a and b) and did not increase on top of clay-enriched horizons, which is indicative of negligible vertical and lateral translocation of both.

The presence of BC in the weathered subsoil (Bw) and the clay accumulation horizon (Bt) of the Elsbach Valley (Fig. 3c) and the Tönchesberg (BtAh of MIS 5a; Fig. 3b) may support findings by Brodowski et al. (2007), Hammes et al. (2008b), Rodionov et al. (2010) and Knicker et al. (2006, 2012) that there may be a vertical translocation of BC and/or direct formation of BC within the former subsoils from charred roots (Knicker et al., 2006, 2012). However, even more likely is that these subsoil horizons were mixed with older topsoil material or were even exposed to the surface due to reworking on the slopes (Boenigk and Frechen, 2001; Schmidt et al., 2011). Yet, the BC content in the Bt horizons did not parallel the enrichment in clay, i.e. BC input via charring or soil sediment mixing might be a more relevant input than colloidal transport with clay illuviation. Besides, there was no BC in the clay accumulation horizon (Bt) of Koblenz–Metternich (Fig. 3a). We conclude that translocation of BC with clay minerals was likely only of minor contribution to the depth distribution of BC. The lack of BC in the pure loess also strongly supports the assumption that there was no significant leaching of BC in a dissolved form.

4.2. BC as a proxy for fire regime

The amount and quality of BC production may depend on the burning ecosystem. Czimczik and Masiello (2007) outlined, for instance, that high BC production may be found under prairie grass vegetation, whereas in boreal forests BC production is lower and in both, BC may partly be lost due to re-burning. This is corroborated by results of Wang et al. (2005, 2012) who found elevated BC concentration in periods with a cold and dry climate related to grass vegetation in tundra-like ecosystems. In contrast, deciduous forests are not likely to burn frequently on a large spatial scale (Pyne et al., 1996; Thonicke et al., 2010; Marlon et al., 2013). The timespan covered in the sequences here – covering Eemian to Middle Weichselian palaeosols – was prone to severe change in temperature and vegetation. The enrichment in BC in sediments of MIS 5b and MIS 5c occurred when initially tundra-like vegetation and then a pine-birch-abies population was prevalent (Behre and Lade, 1986). The beginning of MIS 4 was likely accompanied by a shift from the MIS 5a forest or forest steppe to tundra-like vegetation. The sediments of the beginning MIS 4 have, however, likely received their humus and BC contents from the erosion of the MIS 5a soils on the slope (Fig. 3a; Boenigk and Frechen, 2001; Schmidt et al., 2011).

The B5CA/B6CA ratio (BC quality) allows reconstruction of fire temperature and a study of differences in the prevalent fire regime (Schneider et al., 2013; Wolf et al., 2013). A literature compilation by Wolf et al. (2013) revealed that forest and grass dominated ecosystems burn at comparable temperatures frequently around 285 °C ± 143 °C, leading to representative BPCA patterns in natural charcoal (B5CA/B6CA for grass derived charcoal > 0.8; Wolf et al., 2013). Accordingly, B5CA/B6CA values of ca. 0.95 for all Ah and humic-rich horizons indicated that a "cold" burning of grass and leaves, pointing to tundra and forest steppe vegetation (Schneider et al., 2011; Wolf et al., 2013), dominated in the lower Weichselian. Also, the palynological data from these periods indicated that ecosystems changed from tundra-like to forest in the MIS 5 to MIS 4 transition (Behre and Lade, 1986).

In the sequences we observed changes in BC quantity but not in quality due to (i) indifferent B5CA/B6CA values for forest (leave) fires and grass fires (Wolf et al., 2013) and (ii) due to mixing of the soil sediments on the slope. Nevertheless, compared with B5CA/B6CA values > 1.5 for pure, lab produced charcoal, the results for the BC quality in palaeosols may have two further implications. Either the BC quality changed during storage in the last 130 ka, i.e. we may only interpret relative differences with time in the B5CA/B6CA pattern as indicators for changing combustion temperature, but not the absolute temperature as suggested by, e.g. Schneider et al. (2013). Or, preferentially the char that accumulated derived from high temperature burning, such as from soot formed in the gas phase and transported across large distances, whereas the grass and leaf charcoal was more degraded or did not reach the deposit. Interpreting changes in BC quality within terrestrial archives therefore remains a challenge, and is restricted to the assessment of relative differences in BC quality and undisturbed palaeosols. In any case, the BPCA analysis clearly showed that natural fires were abundant during the MIS 5, equivalent to about 65–128 ka ago.

5. Conclusions

Loess–palaeosol sequences in Central Europe provided an insight into past fire regimes from tracing BC content and quality. We were able to detect BC in all palaeo-topsoil horizons. The amounts were comparable to modern natural fire residues in soil, suggesting that at these warm phases fires were abundant. We also conclude that this BC was preserved for > 100,000 yr. BC input at three sites from different local environmental contexts was comparable, indicating that the BPCA method reflects past regional burning conditions.

Nevertheless, we detected only little variation in BC quality. On one hand this was due to the lack of sensitivity of the BPCA method for distinguishing grass fires from forest fires. On the other hand, however, the B5CA/B6CA values were lower than those attributed to lab-produced charcoal, assuming that in soils BC occurs as a mixture of charcoal and soot BC or that more stable BC forms preferentially survived in the soils. In any case, reconstructing fire temperature from charcoal analysis in terrestrial archives is promising but must be considered with care.

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