Black carbon contributes to organic matter in young soils in the Morteratsch proglacial area (Switzerland)

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Abstract: Most glacier forefields of the European Alps are being progressively exposed since the glaciers reached their maximum expansion in the 1850s. Global warming and climate changes additionally promote the exposure of sediments in previously glaciated areas. In these proglacial areas, initial soils have started to develop so that they may offer a continuous chronosequence from 0 to 150-yr-old soils. The build-up of organic matter is an important factor of soil formation, and not only autochthonous but also distant sources might contribute to its accumulation in young soils and surfaces of glacier forefields. Only little is known about black carbon in soils that develop in glacier forefields, although charred organic matter could be an important component of organic carbon in Alpine soils. The aim of our study was to examine whether black carbon (BC) is present in the initial soils of a proglacial area, and to estimate its relative contribution to soil organic matter. We investigated soil samples from 35 sites distributed over the whole proglacial area of Morteratsch (Upper Engadine, Switzerland), covering a chronosequence from 0 to 150 yr. BC concentrations were determined in fine earth using the benzene polycarboxylic acid (BPCA) marker method. We found that charred organic matter occurred in the whole area, and that it was a main compound of soil organic matter in the youngest soils, where total Corg concentrations were very low. The absolute concentrations of BC in fine earth were generally low but increased in soils that had been ex- posed for more than 40 yr. Specific initial microbial communities may profit from this additional C source during the first years of soil evolution and potentially promote soil development in its early stage.

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Abstract

Most glacier forefields of the European Alps are progressively exposed since the glaciers reached their maximum expansion in the 1850s. Global warming and climate changes additionally promote the exposure of sediments in previously glaciated areas. In these proglacial areas, initial soils have started to develop so that they may offer a continuous chronosequence from 0 to 150 year-old soils.

The build-up of organic matter is an important factor of soil formation, and not only autochthonous but also distant sources might contribute to its accumulation in young soils and surfaces of glacier forefields. Only little is known about black carbon in soils that develop in glacier forefields, although charred organic matter could be an important component of organic carbon in Alpine soils.

The aim of our study was to examine whether black carbon is present in the initial

soils of a proglacial area, and to estimate its relative contribution to soil organic matter. We investigated soil samples from 35 sites distributed over the whole proglacial area of Morteratsch, covering a chronosequence from 0 to 150 years. BC concentrations were determined in fine-earth using the benzene polycarboxylic acid (BPCA) marker method. We found that the proportion of BC to total C_{org} was related to the time since the surface was exposed. Soils on surfaces exposed less than 40 years ago contained the highest proportion of BC. The absolute concentrations of BC in fine-earth were generally low but increased in soils that had been exposed for more than 40 years.

Charred organic matter occurred in the whole area, and it was a main compound of soil organic matter in young soils, where total C_{org} concentrations were very low. Specific initial microbial communities consequently may profit from this additional C source during the first years of soil evolution and potentially promote soil development in its early stage.

Keywords: black carbon, BPCA, soil organic matter, glacier forefield, chronosequence, soil development

1. Introduction

Alpine glacier forefields, or proglacial areas, are defined as the area between the present-day glacier front and the terminal moraines deposited in the 1850s, when the glaciers reached their maximum expansion. The most evident developments in Alpine soil formation occur in proglacial areas where new soils form after glaciers retreat and recently formed soils are continuously developing (Egli et al., 2006). Increasing temperatures will lead to a further retreat of glaciers and additional areas will become subject to weathering and formation of soil organic matter. Proglacial

environments are also important for the understanding of global CO_2 cycling on glacial/interglacial timescales as they made up a significant amount of the global land surface during the Quaternary due to the advance and retreat of glaciers and ice sheets (Gibbs and Kump, 1994).

Retreating glaciers often expose barren substrates that become colonised by organisms, beginning the process of primary plant succession which affects the evolution of organic matter in the developing topsoils (Burga et al., 2010). Not only autochthonous but also distant (allochthonous) sources may contribute to the accumulation of soil organic carbon (C_{org}) in young soils and surfaces of glacier forefields. Among these sources are dry and wet atmospheric deposition, faecal deposit, ground-nesting of birds, soot deposit, input due to photo-autotroph organisms, or organic matter of fossil (and preserved) soils (e.g. Bauer et al., 2002; Kim et al., 2005; Arimitsu et al., 2007; Mindl et al., 2007; Xu et al., 2009; Bogdal et al., 2011; Kim et al., 2011; Wientjes et al., 2011). Bernasconi et al. (2011) demonstrated that soil organic matter in initial soils of the Damma glacier forefield contains a relatively high proportion of labile organic compounds which are easily oxidisable and have a short turnover time (annual to decadal). Autochthonous recalcitrant organic matter is not formed in significant amounts in this environment at decadal time scales.

Bardgett et al. (2007) measured changes in the composition of microbial communities and their use of carbon compounds along a 150-year chronosequence in the Austrian Alps. They found that the initial soil microbial communities of the youngest sites were heterotroph organisms that used previously buried recalcitrant carbon, e.g. black carbon, as an energy source. On older sites, after 50 years of exposure, the soil microorganisms respired modern carbon that derived from modern plant growth.

Charred organic matter and soot, or compounds of black carbon (BC), that are released during vegetation fires or fossil fuel burning are ubiquitous components of soils. Several studies demonstrated that BC can be an important compound even in Alpine soils (Bucheli et al., 2004, Eckmeier et al., 2010) or Alpine lake sediments (Bogdal et al., 2011), and in glacial ice cores (Lavanchy et al., 1999; Thevenon et al,. 2009), either due to in-situ burning of biomass or via atmospheric deposition. Glaciers can be sources of BC, when they release BC with glacial runoff water that has been incorporated into the ice after melting (Stubbins et al., 2012).

Although the build-up of organic C is an important factor governing the formation of soils and weathering, only very little is known about the presence of BC in very young soils that are developing in glacier forefields. To analyse time trends in such areas, the study of soil chronosequences is an important tool to derive short- to long-term formation rates. The aim of our research was to examine whether BC is an allochthonous source of soil organic matter in the young soils that develop in the proglacial area of the Morteratsch glacier (Upper Engadine, Switzerland) and to estimate its relative contribution (as a function of time) to total organic matter in soils.

2. Materials and methods

2.1 Investigation area

We investigated soils and sediments of the glacier forefield Morteratsch in the Upper Engadine (Switzerland), which is limited by the terminal moraines that have been deposited during the 'Little Ice Age' in the 1850s (Fig. 1). The recent length of this proglacial area is approx. 3 km and it has an area of 1.8 km^2. The proglacial area is situated in a valley that runs N to S, in an altitude of 1900 m asl to about 2050 m asl. Present climatic conditions are approx. 0.5 °C mean annual temperature and approx. 1000-1300 mm mean annual precipitation (calculated from data from the

meteorological stations Samedan and Bernina). The history of the Morteratsch glacial environment has been studied extensively in geomorphologic and climatic studies (cf. Burga and Perret, 1998; Magny, 1992; Maisch, 1992; Renner, 1982; Gamper, 1985; Fitze, 1982; Patzelt, 1977). The glacial till in the glacier forefield represents the parent material of soil formation. It consists of granitoid and gneissic rock material which underwent a 'green schist' metamorphic event during the high Alpine orogenesis (Büchi, 1994; Spillmann, 1993; Trommsdorff and Dietrich, 1999). Glacial transportation lead to a relatively homogeneous distribution of parent material in the proglacial area.

According to Burga et al. (2010), primary plant succession of the proglacial area started about 7 yr after deglaciation with the Epilobietum fleischeri plant community which includes the species *Epilobium fleischeri, Oxyria digyna* (only in initial stages), *Linaria alpina, Saxifraga aizoides,* and *Rumex scutatus*, and which covered larger areas after about 27 yr. First larch trees, willow and green alder shrubs and the first dwarf-shrubs (e.g. the rust-leaved alpenrose) appeared on areas which have been ice-free for about 12–15 years. Larch-Swiss stone pine stands (Larici-Pinetum cembrae) needed more than 150 yr to establish. Only small patches of Larici-Pinetum cembrae can be found on the proglacial area while they are dominant in adjacent areas. The succession was not a linear process and influenced by various micro-site dependent factors like soil moisture, grain size, local disturbances or micro-climate that led to a patchy distribution of plant communities.

The dominant soil units (some sites do not have a soil) in the proglacial area are Haplic Fluvisols (Endoskeletic), Skeletic or Lithic Leptosols and Humi-skeletic Leptosols, and Dystric and Endogleyic Cambisols (endoskeletic) (IUSS working group, 2006). The youngest soils showed almost no morphological signs of chemical weathering and alteration products. The development of soils in the Morteratsch area

131 during 150 years of surface exposure, including soil organic matter formation and
132 mineral weathering processes, have been studied in detail (e.g. Egli et al., 2010;
133 Mavris et al., 2010).
134
135 *2.2 Methods*
136 Two sets of samples were investigated that had been taken from the whole proglacial
137 area and that cover a chronosequence ranging from 0 to 150 yr (Table 1). Samples
138 S1-10 are ten topsoil samples (soil depth between 1 to max. 12 cm) from ten sites,
139 which are shown in Fig. 1. Close to these sites, material from soil pits has been
140 analysed in detail (Mavris et al., 2010). Samples AS1-29 were sampled from
141 additional sites of the proglacial area at a depth of 0-5 cm.
142 All samples have been dried at 105°C, sieved (< 2mm) and ball-milled for further
143 analysis.
144 Total C, nitrogen (N) and hydrogen (H) contents were measured using a C/H/N
145 analyzer (Elementar Vario EL). The organic matter content was determined
146 gravimetrically after dry combustion in a muffle furnace at 550 °C for 6 h (Nocentini et
147 al., 2010). The oxygen (O) content was calculated from the measured data. Total C
148 was considered as organic C (Corg) because $CaCO_3$ could not be detected in any
149 sample using HCl and only traces (< 0.5%) – if ever – could be observed in DRIFT
150 spectra. The soil is acidic (pH < 6) in the whole proglacial area (Mavris et al. 2010).
151 The concentration of black carbon (BC) in fine-earth samples was determined as
152 benzene polycarboxylic acids (BPCA) according to the method described by
153 Brodowski et al. (2005). The samples (two replicates) were first treated with
154 trifluoroacetic acid (TFA) to remove polyvalent cations and then digested with HNO_3
155 at 170 °C for eight hours. The sum of BPCAs in each sample was determined after
156 derivatisation on a gas chromatograph equipped with a flame ionisation detector

157 (GC-FID). The patterns of benzene rings is dependent on the degree of condensation
158 of the polyaromatic carbon compounds. We used a conversion factor of 2.27 to
159 estimate BC contents from total BPCA-C concentrations. The factor provides a
160 conservative minimum estimate of the true BC contents in soil (Glaser et al., 1998;
161 Brodowski et al. 2005).
162 Environmental scanning electron microscopy (ESEM) and energy-dispersive
163 spectroscopy (EDS) were performed on three loose granular samples (uncoated) (AS
164 21, 24, 28) at the Institute for Building Materials (ETH Zurich, Switzerland). The fine-
165 earth fraction of the samples was washed with deionized water and the floating
166 material (density < 1 g/cm^3) was collected and air-dried. This enabled the selective
167 extraction of the organic fraction of the sediment, including charcoal material. The
168 analysis was performed using a Dual Beam Quanta 200 3D FEI coupled with EDX,
169 with Dual BSD detector and W emitter operating at an accelerating voltage of 20 kV.
170 The EDS detector is equipped with an ultra-thin window allowing detection of mineral
171 elements and carbon, which provided the elemental composition of the solid phases.
172 Soil colour was measured for dried and homogenised soil samples in triplicates using
173 a spectrophotometer (Konica Minolta CM-5) by detecting the diffused reflected light
174 under standardised observation conditions (2° Standard Observer, Illuminant C). The
175 colour spectra were obtained in the 360 to 740 nm range, in 10 nm increments.
176 The spectral information was converted into the Munsell colour system and the
177 CIELAB Color Space (CIE 1976) using the Software SpectraMagic NX (Konica
178 Minolta). The L* values indicate the extinction of light, or luminance, on a scale from
179 L* 0 (absolute black) to L* 100 (absolute white).
180

181 **3. Results**

182 *3.1 Organic C and nitrogen*

183 The C_{org} concentrations ranged from 1.9-131.0 g kg^{-1}, with an average of 23.6 and a
184 median of 11.5 g kg^{-1} (Table 2). Figure 2 shows that the C_{org} concentrations in
185 younger soils did not exceed 5 g kg^{-1} while after about 40 years of surface exposure,
186 the C_{org} concentrations increased and reached values close to 80-100 g kg^{-1} after
187 about 60 years, and a maximum of 131 g kg^{-1} at 75 years. There is, however, a
188 strong scatter of C_{org} concentrations that is not only related to the factor time but also
189 to others such as vegetation. The average C_{org} concentrations were higher under the
190 pioneer grass communities (46 g kg^{-1}, 10 sites; vegetation type 2 in Table 1) than
191 under the Epilobietum fleischeri sites (17 g kg^{-1}, 15 sites; vegetation type 3). Only
192 three sites were covered by plants belonging to the green alder scrub communities
193 (Alnetum viridis), they reached an average of 15 g kg^{-1}.
194 The N concentrations ranged from 0.2 to 7.0 g kg^{-1} (mean 1.3, median 0.8 g kg^{-1}).
195 The C/N ratios were between 2 and 58 (mean 19, median 15). For the samples S1-
196 10 that were taken only from topsoil the C/N ratio was between 12 and 36. The
197 distribution of N shows a close relation to the vegetation type, only five sites contain
198 more than 1.4 g N kg^{-1}, of which four are covered by pioneer grass communities
199 (Geo montani-Nardetum and Poion alpinae, vegetation type 2) and one by green
200 alder scrub communities (Alnetum viridis, vegetation type 4).
201
202 *3.2 Black Carbon*
203 The BC concentrations (calculated with a conversion factor from BPCA-C) varied
204 between 0.2 and 5.6 g kg^{-1}, with an average mean of 1.0 and a median of 0.5 g kg^{-1}
205 (Table 2). Since the BPCA-C yield exceeded 1.2 g kg^{-1} C_{org} (without conversion
206 factor), we can exclude competing biogenic sources that could significantly add to the
207 BC concentrations (Brodowski et al., 2005).
208 The concentration of BC is higher in soils that have been developing since more than

40 years, as is the C_{org} concentration. The BC and C_{org} concentrations were highly correlated (R^2 = 0.89, $p<0.001$). The proportion of BC to total C_{org} was between 23 and 137 g BC kg^{-1} C_{org} (mean 50, median 46 g BC kg^{-1} C_{org}). Excluding sample AS6, which was considered an outlier, the relationship with time of surface exposure reaches R^2 = 0.4 on a logarithmic scale (y = -16.4ln(x) + 114.35), as shown in Fig. 3. The youngest soils (< 40 years) contained the highest proportion of BC (68-118 g BC kg^{-1} C_{org}), while C_{org} concentrations were low (2-4 g kg^{-1}).

The relative distribution of B6CA (6 carboxyls) to total BPCAs was 25% in average, with a tendency to larger amounts of B6CA in older sites (Fig. 4). The patterns of benzene rings were similar for all samples, with the exception of AS6 where the proportion of B6CA reached 50 %.

3.3 Atomic ratios O/C and H/C

The O/C ratios varied from 0.0 to 1.3, the H/C ratios from 0.1 to 2.8. There was no significant relation between O/C ratios and BC concentrations or the proportion of BC at C_{org}. The position of the samples in the van Krevelen plot in Fig. 5 (after Kim et al. 2003) showed that the average atomic ratios for most age groups are typical for plant lignin or cellulose material, with the exception of the youngest age group (0-20 yrs) that was characterized by lower H/C ratios.

3.4 ESEM-EDS

ESEM-EDS allowed the identification of charcoal particles based on their morphology and elemental composition in all analysed samples (AS 21, 24, 28), as shown in Fig. 6. The visual identification was supplemented with the measurement of the atomic ratios of the particles. Following Brodowski et al. (2005), we considered BC as particles that had an O/C ratio of ≤0.33 (Stoffyn-Egli et al., 1997) on at least one point

of an observed particle.

3.5 Soil Colour

Soil colour, in particular the Luminance, or brightness, of the soil colour (L*), varied between 38 and 70 (mean 54, median 55). It was correlated both to C_{org} (R^2 = 0.545, $p<0.001$) and BC concentrations (R^2 = 0.462, $p<0.001$), but not to time.

4. Discussion

Although the environmental conditions in the Morteratsch proglacial area are relatively homogeneous, small scale variability affects soil properties. This is reflected, among others, in the C_{org} concentrations which considerably varied after 30 to 40 years of soil evolution. Small changes such as water content of the substrate, the micro-relief and micro-climate seem to be crucial for both the development of the vegetation and, consequently, also the early evolution of the soils. Two vegetation types persisted over large parts of the chronosequence: pioneer grass communities (Geo montani-Nardetum and *Poion alpinae,* vegetation type 2) and *Epilobietum fleischeri* with single willow shrubs and Alpenrose (vegetation type 3). The C_{org} and N concentrations were affected by these differences in vegetation, the average concentrations were highest under the pioneer grass communities. Oehl et al. (2011) found, for example, that *Epilobium fleischeri* is strongly arbuscular mycorrhizal, but plants in closest distance to the glacier were non-mycorrhizal which finally also influences the C/N ratio in a soil.

Due to the temporal trend, the variability of soil organic matter under all vegetation types was high. The soil colours reflected the heterogenity of soil formation. Due to their low evolution stage, the soils had a relatively light colour but darkened progressively with increasing C_{org} and BC contents (cf. Eckmeier et al., 2010). The

261 yellow hues showed that the soils were not affected by soil forming processes as
262 brunification yet.
263 BC was present in the whole investigated area, independent from the time since the
264 surface has been exposed, although the concentrations were very low in the
265 youngest soils. The occurrence of BC in remote mountainous environments is not
266 unusual. BC, or, more generally, combustion residues that have been transported as
267 aerosols were deposited on the surfaces of Tibetan glaciers (Xu et al. 2009).
268 Stubbins et al. (2012) found that fossil dissolved organic matter in runoff water of
269 glaciers in Alaska was dominated by aerosols produced during combustion, and that
270 these are a major element in the carbon cycle of glacial environments. BC is also
271 commonly found in the Alpine environments of Switzerland. In the sediments of
272 Lakes Thun, Engstlen and Oberaar, up to one-third of C_{org} was BC (determined by
273 CTO-375; Bogdal et al., 2011). The analysis of ice cores from Colle Gnifetti showed
274 that the deposition of BC increased strongly since the end of the 19^{th} century
275 (Thevenon et al., 2009). The same trend was measured for polycyclic aromatic
276 hydrocarbons (PAHs), which are also produced during burning and which are likely to
277 be absorbed at BC particles. PAH concentrations reached a maximum 1945-1955,
278 and then decreased again. A source assignment using specific PAHs indicated that
279 the ratio of wood and coal burning in contrast to fossil fuel combustion decreased
280 until the 1980s, then the trend reversed (Gabrieli et al., 2010).
281 The source of BC measured in the Morteratsch forefield is charcoal or diagenetic
282 coal. Charcoal particles were found by microscopic inspection, and the BPCA pattern
283 correspond to BPCA pattern of charcoal and coal as described by Roth et al. (2012).
284 The BPCA method, however, would also underestimate the amounts of soot-derived
285 BC (Hammes et al., 2007). Potential sources for the BC in the Morteratsch proglacial
286 area would be wood combustion for heating, charcoal kilns which have been

287 common in the area until the 20th century, or the railway (Rhaetische Bahn) which is
288 passing in a distance of about 2.5 km from the glacier front that had been equipped
289 with a steam engine until the 1920s.
290 In two rural areas of Switzerland and in the city of Zurich, burning of wood produced
291 up to one-third of BC emissions (measured during 2.5 years on aerosols using a
292 spectroscopic method) during the winter and 2-10% during summer (Herich et al.,
293 2011). Szidat et al. (2007) even reported contributions of up to 88% of residential
294 wood burning on particulate matter in Alpine valleys during winter. The analysis of
295 104 soil samples from the Swiss soil monitoring network showed that the BC
296 concentrations had a very uniform distribution because of the uniform deposition of
297 the atmospherically transported BC aerosols (Agarwal & Bucheli, 2010).
298 Up to now, BC concentrations have not been measured in initial soils of glacier
299 forefields. A small decrease in the proportion of aromatic C with soil age has been
300 found in the Damma glacier forefield using ^{13}C-NMR (Dümig et al., 2011), while the
301 proportion of aromatic C in soil organic matter of the Morteratsch glacier forefield,
302 measured using DRIFT, was increasing with time of exposure (Egli et al., 2010). This
303 increase in aromatic compounds was, however, not related to fire-derived organic
304 matter, but rather indicated the presence of condensed and lignin-derived
305 compounds (Poirer et al., 2003).
306 Charred organic matter was deposited over the whole proglacial area. Local fires
307 could have influenced specific sites, especially S9 where the absolute BC
308 concentration was considerable, or AS6 where the proportion of BC at C_{org} and the
309 proportion of B6CA were highest. The amount of B6CA is slightly but not significantly
310 higher in samples on older surfaces. The youngest soils are characterised by very
311 low C_{org} concentrations, which resulted in a higher proportion of BC in these soils.
312 This is reflected by the H/C ratios which are rather low in the youngest soil samples.

313 Here, specific initial microbial communities consequently may profit from this
314 additional C source during the first years of soil evolution, as was shown for the
315 Austrian Alps by Bardgett et al. (2007), and potentially promote soil development in
316 its early stage.
317

318 **5. Conclusion**

319 The developing soils in the Morteratsch proglacial area contained charred organic
320 matter, most likely derived from charcoal or coal, which was distributed over the
321 entire investigated area. It is, however, not known if all BC was deposited by
322 atmospheric deposition, or if the source of BC was material that has accumulated on
323 the glacier and was deposited on the parent material or soil after the ice finally
324 melted. BC concentrations were lowest on surfaces that were exposed during the last
325 40 years, either due to their lower exposure time or to a reduced input of BC during
326 the last 40 years. BC contributed to total C_{org} which is particularly important at initial
327 soil formation stages, where microorganisms could have used BC as a C source
328 whereas other C_{org} sources provided by vegetation were still scarce or simply lacking.
329

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336

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Tables

Table 1. General properties of the investigated sites in the proglacial area.

Site	Year of exposure	Exposure time	Horizon	Depth	Skeleton	Soil type (WRB)	Vegetation[a]
		yr		*cm*	*wt-%*		
S1	1870	140	A	0-6	41	Humi-skeletic Leptosol	4
AS1	1870	140	A	0-5	n.d.	Humi-skeletic Leptosol	2
S2	1880	130	A	0-10	64	Humi-skeletic Leptosol	4
AS2	1880	130	A	0-5	n.d.	Humi-skeletic Leptosol	2
AS3	1890	120	A	0-5	n.d.	Humi-skeletic Leptosol	5
AS4	1890	120	A	0-5	n.d.	Skeletic Leptosol	2
S3	1900	110	A	0-5	54	Humi-skeletic Leptosol	3
AS5	1900	110	A	0-5	n.d.	Skeletic Leptosol	7
S4	1910	100	A	0-1	55	Humi-skeletic Leptosol	3
AS6	1910	100	AC	0-5	n.d.	Skeletic Leptosol	2
AS8	1920	90	AC	0-5	n.d.	Skeletic Leptosol	6
S10	1930	80	A1	0-2	49	Humi-skeletic Leptosol	3
AS9	1930	80	AC	0-5	n.d.	Skeletic Leptosol	4
S9	1935	75	O	0-3	44	Humi-skeletic Leptosol	2
S5	1940	70	A1	0-1	7	Humi-skeletic Leptosol	2
AS10	1940	70	A	0-5	n.d.	Humi-skeletic Leptosol	2
AS11	1945	65	A	0-5	n.d.	Humi-skeletic Leptosol	3
AS12	1945	65	A	0-5	n.d.	Skeletic Leptosol	3
S8	1950	60	O/A	0-12	63	Skeletic Leptosol	2
AS13	1950	60	A	0-5	n.d.	Skeletic Leptosol	3
AS14	1950	60	A	0-5	n.d.	Humi-skeletic Leptosol	3
S6	1960	50	A	0-3	64	Skeletic Leptosol	3
S7	1960	50	A	0-4	26	Skeletic Leptosol	2
AS15	1965	45	A	0-5	n.d.	Skeletic Leptosol	2
AS16	1965	45	(A)C	0-5	n.d.	Skeletic Leptosol	3
AS17	1970	40	AC	0-5	n.d.	Skeletic Leptosol	3
AS18	1970	40	AC	0-5	n.d.	Skeletic Leptosol	3
AS19	1975	35	(A)C	0-5	n.d.	-	3
AS20	1975	35	(A)C	0-5	n.d.	-	3
AS21	1975	35	(A)C	0-5	n.d.	-	3
AS22	1980	30	(A)C	0-5	n.d.	-	0
AS23	1980	30	(A)C	0-5	n.d.	-	3
AS24	1990	20	(A)C	0-5	n.d.	-	0
AS28	2007	3	C	0-5	n.d.	-	0
AS29	2007	3	C	0-5	n.d.	-	0

n.d. = not determined

[a] 0 = no vegetation; 2 = Pioneer grass communities (Geo montani-Nardetum and Poion alpinae); 3 = Epilobietum fleischeri with single willow shrubs and Alpenrose; 4 = Green alder scrub (Alnetum viridis) (*Alnus viridis* and tall perennial herbs, *Salix spec., Poa spec., Deschampsia caespitosa, Avenella flexuosa, Nardus stricta, Festuca spec., Phleum rhaeticum, Anthoxanthum alpinum, Calamagrostis villosa*); 5 = Grass heath on moister soils (grass species e.g. *Festuca violacea, Calamagrostis villosa, Phleum rhaeticum, Poa alpina*); 6 = Boulder plant communities, partially Epilobietum fleischeri (*Epilobium fleischeri, Adenostyles leucophylla, Rumex scutatus, Dryopteris spec., Athyrium spec., Gymnocarpium dryopteris, Polystichum lonchitis*); 7 = Rock vegetation (e.g. *Agrostis rupestris, Silene rupestris, Sempervivum arachnoideum*)

519 Table 2. Spectral and chemical properties of the fine-earth fraction (< 2mm).

Site	Exposure time	Lumi-nance	Munsell colour			C_{org}	N	C/N	O/C	H/C	BC [a]	BC [a]	B6CA
	yr	*L**	*Hue*	*Value*	*Chroma*	*g kg^{-1}*	*g kg^{-1}*	*Weight ratio*	*Atomic ratio*		*g C kg^{-1} Corg*	*g kg^{-1}*	*%*
S1	140	57.9	2.5 Y	5.6	1.5	7.1	0.6	12	0.7	1.0	49.7	0.4	27.8
AS1	140	47.5	1.6 Y	4.6	1.5	61.2	4.6	13	0.6	1.8	43.1	2.5	26.3
S2	130	40.2	0.8 Y	3.9	1.1	64.1	3.0	22	0.5	0.8	43.2	2.8	22.8
AS2	130	48.1	2.2 Y	4.7	1.8	18.1	1.2	15	0.5	1.6	48.8	0.8	19.5
AS3	120	58.3	2.9 Y	5.7	1.5	7.3	0.3	23	0.7	0.3	54.5	0.4	43.9
AS4	120	54.8	2.3 Y	5.3	1.7	9.4	0.4	24	0.8	0.4	49.9	0.5	38.5
S3	110	51.6	2.3 Y	5.0	1.4	30.3	1.0	29	0.4	1.3	33.1	1.0	27.7
AS5	110	47.2	1.9 Y	4.6	1.7	14.2	1.4	10	1.0	0.7	58.1	0.8	28.4
S4	100	39.0	1.4 Y	3.8	1.5	54.5	1.2	47	0.7	1.7	25.8	1.4	20.7
AS6	100	62.2	3.1 Y	6.1	1.3	3.2	0.7	4	1.3	2.2	136.7	0.4	49.9
AS8	90	63.9	2.5 Y	6.2	1.6	3.9	0.4	10	0.2	1.7	n.d.	n.d.	n.d.
S10	80	38.4	1.4 Y	3.7	1.3	47.9	1.3	36	0.9	1.6	44.9	2.1	14.5
AS9	80	62.6	3.4 Y	6.1	1.4	5.3	0.6	9	1.2	1.5	44.7	0.2	28.8
S9	75	39.4	0.5 Y	3.8	1.4	131.0	7.0	19	0.7	1.6	42.8	5.6	13.5
S5	70	57.1	2.5 Y	5.6	1.1	31.7	0.8	42	0.6	1.1	40.2	1.3	26.1
AS10	70	49.5	2.0 Y	4.8	1.8	29.9	1.1	28	0.5	0.8	61.4	1.8	23.6
AS11	65	49.4	2.1 Y	4.8	1.7	11.6	0.8	14	0.7	0.5	46.6	0.5	24.4
AS12	65	43.8	1.8 Y	4.3	1.6	12.6	0.7	19	0.7	0.4	30.2	0.4	24.1
S8	60	45.1	1.7 Y	4.4	1.2	89.7	3.8	24	0.6	1.5	25.9	2.3	14.8
AS13	60	47.6	2.2 Y	4.6	1.3	11.5	0.4	30	0.5	0.9	27.1	0.3	25.3
AS14	60	58.5	2.7 Y	5.7	1.4	18.1	0.3	58	0.6	1.4	23.7	0.4	22.0
S6	50	48.1	1.4 Y	4.7	1.8	37.0	1.1	34	0.3	1.6	27.9	1.0	33.6
S7	50	43.2	1.6 Y	4.2	1.7	64.5	4.3	15	0.6	1.6	23.0	1.5	21.6
AS15	45	49.7	2.3 Y	4.8	1.6	18.3	0.3	57	0.8	1.6	48.0	0.9	16.6
AS16	45	61.7	2.7 Y	6.0	1.2	4.9	1.4	3	1.2	1.4	46.4	0.2	24.3
AS17	40	58.6	2.2 Y	5.7	1.6	6.0	1.0	6	0.3	1.2	50.1	0.3	23.2
AS18	40	59.1	2.6 Y	5.8	1.5	9.3	0.4	25	0.8	0.9	35.6	0.3	20.4
AS19	35	69.6	2.4 Y	6.8	1.4	2.3	1.0	2	0.2	1.4	n.d.	n.d.	n.d.
AS20	35	59.9	3.0 Y	5.8	1.5	4.1	1.3	3	0.0	1.8	67.7	0.3	22.3
AS21	35	54.7	3.1 Y	5.3	1.5	4.0	0.7	5	0.0	0.1	n.d.	n.d.	n.d.
AS22	30	59.7	3.7 Y	5.8	1.4	2.9	0.3	10	0.3	2.1	69.2	0.2	22.7
AS23	30	64.7	4.2 Y	6.3	1.3	2.6	0.2	11	0.6	0.3	73.7	0.2	22.9
AS24	20	63.8	3.8 Y	6.2	1.4	2.9	0.4	7	0.0	2.2	n.d.	n.d.	n.d.
AS28	3	62.5	4.3 Y	6.1	1.3	1.9	0.7	3	0.9	0.4	117.9	0.2	22.6
AS29	3	60.3	4.5 Y	5.9	1.2	2.1	0.3	8	0.7	2.8	n.d.	n.d.	n.d.

520 [a] Black carbon was calculated by multiplying BPCA-C data with a conversion factor of 2.27 (Brodowski
521 et al. 2005).
522
523

Figure Captions

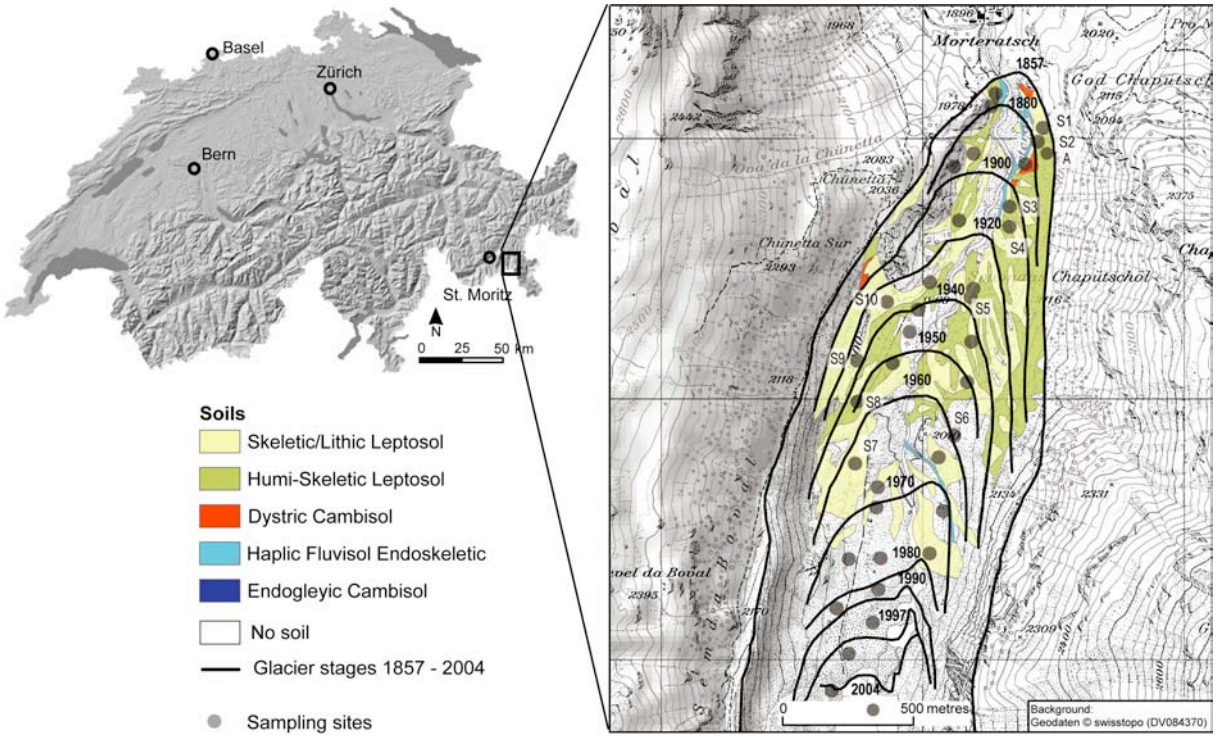
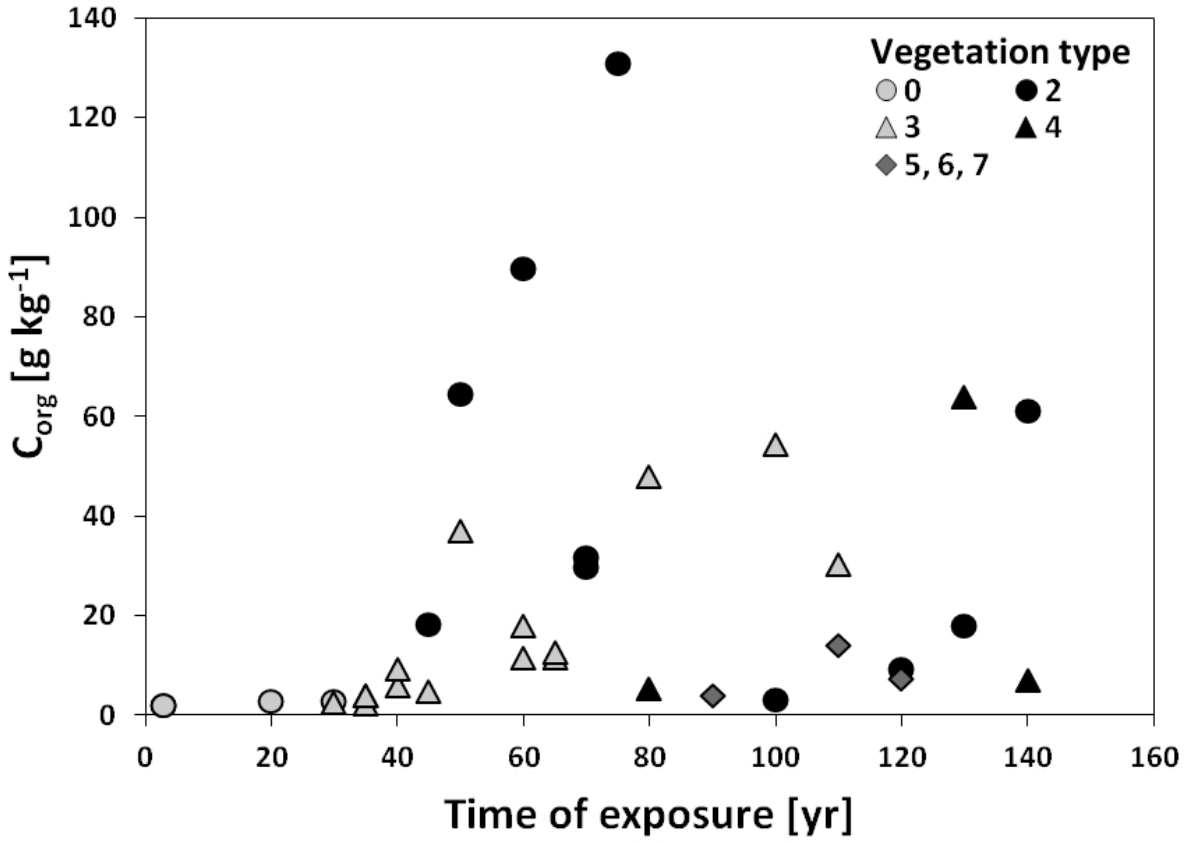


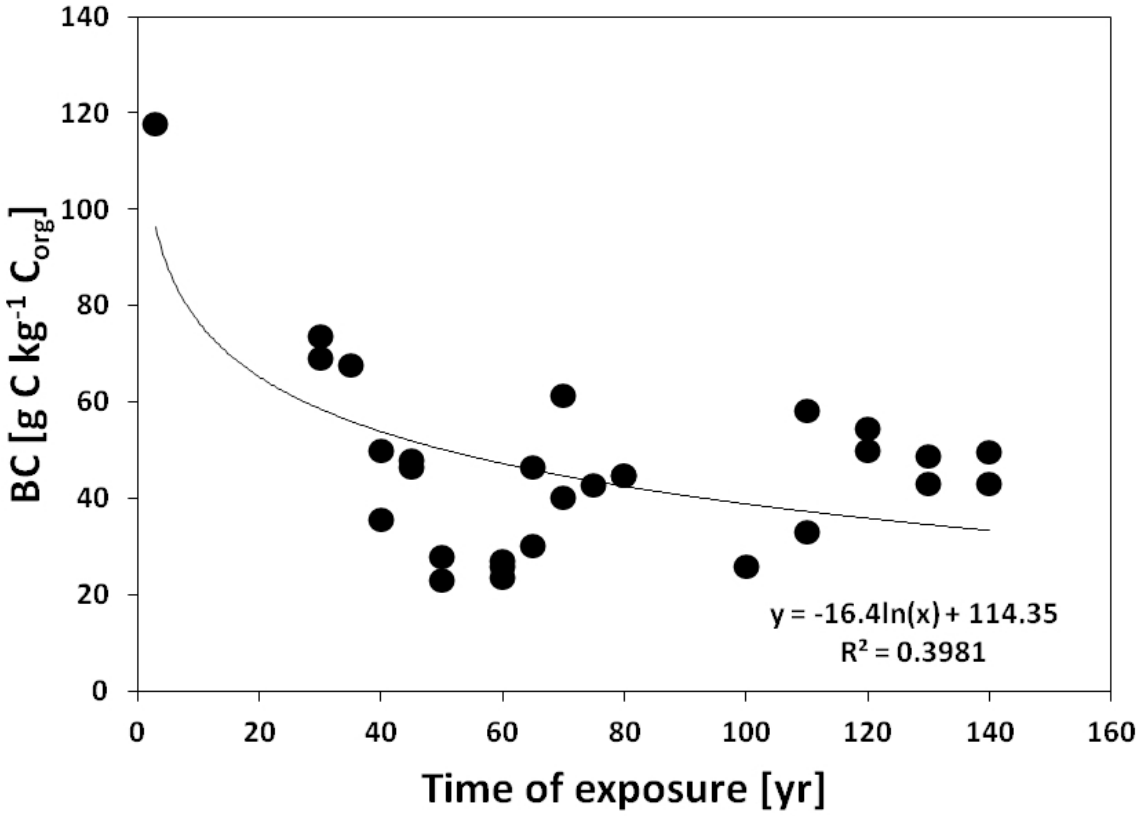
Fig. 1: Location of the Morteratsch glacier forefield with isochrones of glacier retreat, major soil units and position of the topsoil sampling sites, which were analysed in detail regarding soil chemistry and mineralogy (S1–10; Mavris et al., 2010).



529

530 Fig. 2: C_{org} concentrations (in g kg^{-1}) in all samples as a function of surface exposure
531 time and vegetation cover. The vegetation types are related to the numbers given in
532 Table 1.

533

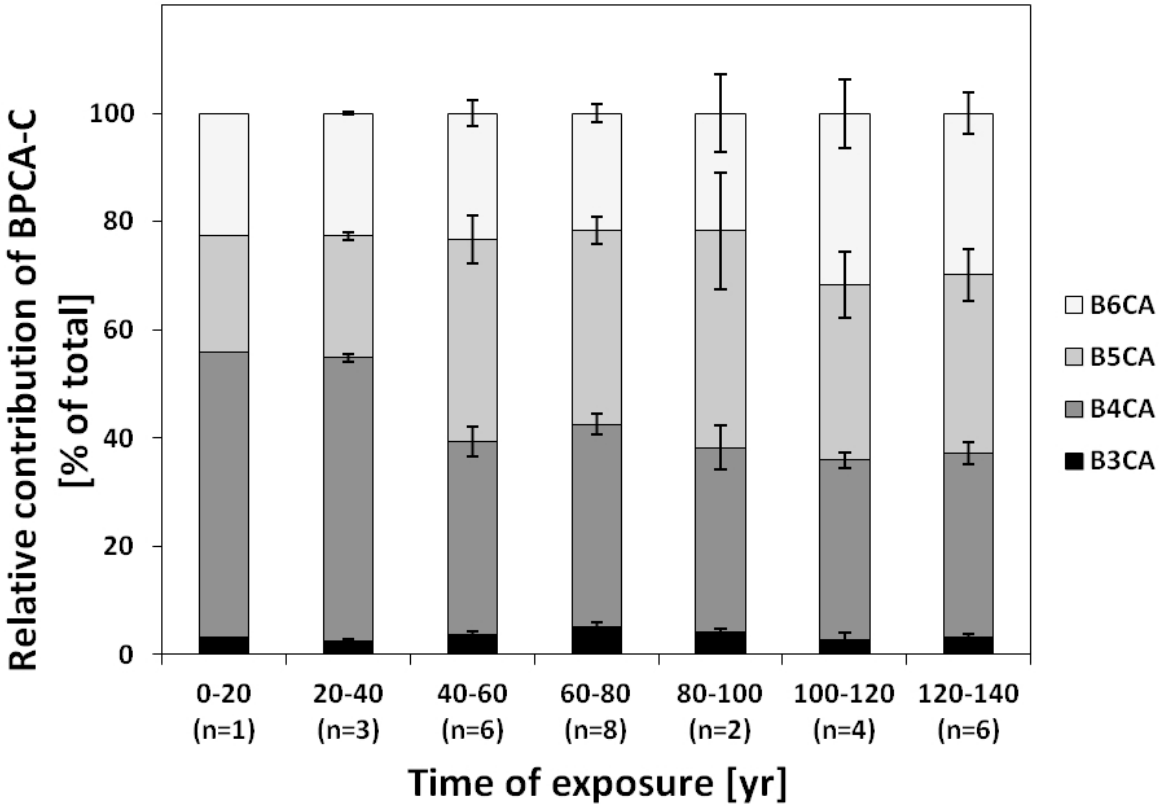


534

535 Fig. 3: Relative proportion of BC in total organic carbon as a function of time for all

536 samples. Sample AS6 was classified as an outlier and removed from the regression.

537

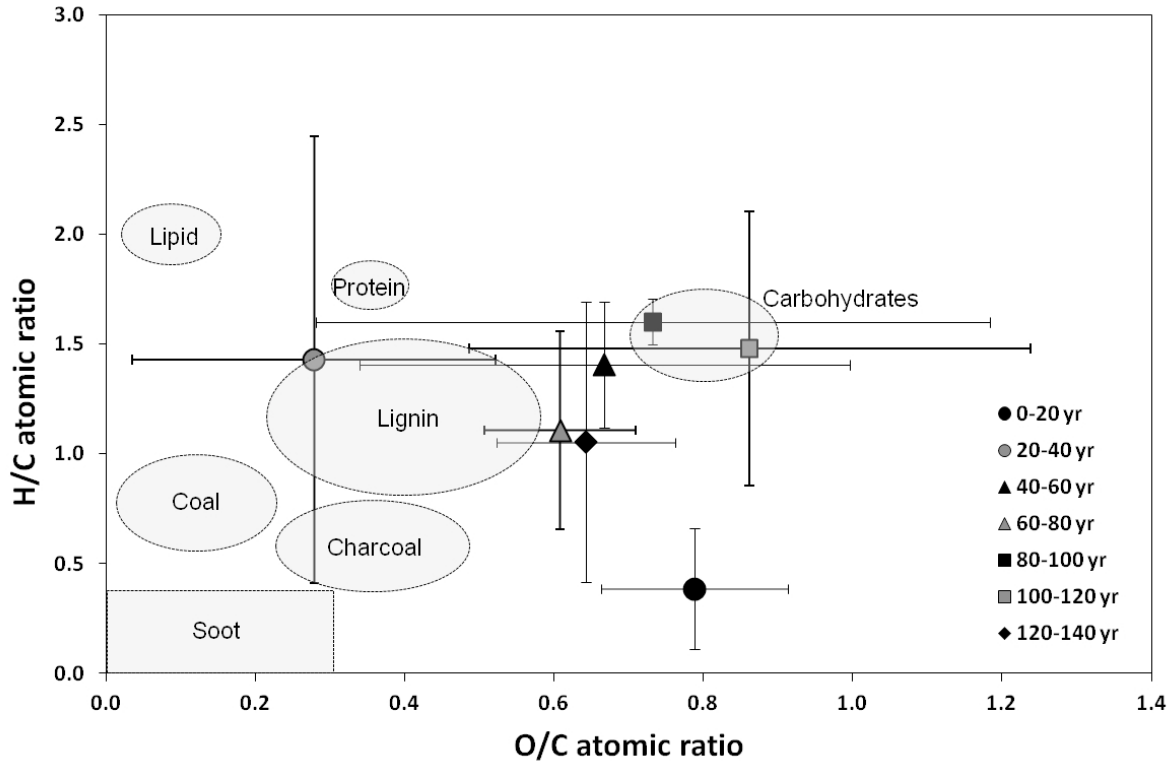


538

539 Fig. 4: Average patterns of benzene rings in proportion to total BPCA-C, showing a
540 trend to larger contributions of B6CA in soil material on older surfaces. Outlier AS6 is
541 included in the age group 100-120. The standard error is given for samples of the
542 corresponding group of time of exposure.

543

544

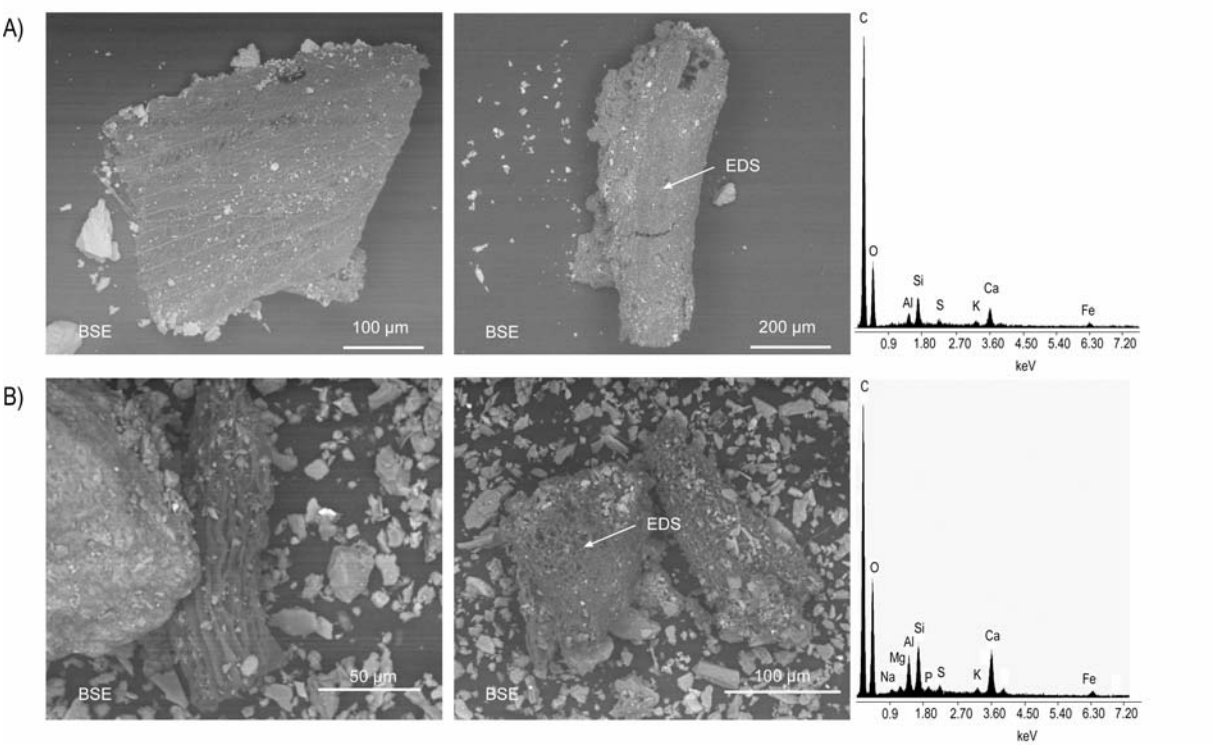


545

546 Fig. 5: Van Krevelen diagram showing the H/C and O/C atomic ratios of soils (mean
547 values ± SD of age classes). Grey shaded areas indicate areas of organic
548 compounds after Kim et al. (2003) and Hammes et al. (2006).

549

550



551

552 Fig. 6: Environmental scanning electron microscopy (ESEM) and energy-dispersive
553 spectroscopy (EDS) on organic particles (charcoal) with a density < 1 g cm^{-3}. A)
554 exposure age three years (AS29); B) exposure age 20 years (AS24). BSE = back-
555 scattered electrons.