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Climate change effects on the stability and chemistry of soil organic carbon pools in a subalpine grassland

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Abstract

Mountain soils stock large quantities of carbon as particulate organic matter (POM) that may be highly vulnerable to climate change. To explore potential shifts in soil organic matter (SOM) form and stability under climate change (warming and reduced precipitations), we studied the dynamics of SOM pools of a mountain grassland in the Swiss Jura as part of a climate manipulation experiment. The climate manipulation (elevational soil transplantation) was set up in October 2009 and simulated two realistic climate change scenarios. After four years of manipulation, we performed SOM physical fractionation to extract SOM fractions corresponding to specific turnover rates, in winter and in summer. Soil organic matter fraction chemistry was studied with ultraviolet, 3D fluorescence, and mid-infrared spectroscopies. The most labile SOM fractions showed high intra-annual dynamics (amounts and chemistry) mediated via the seasonal changes of fresh plant debris inputs and confirming their high contribution to the microbial loop. Our climate change manipulation modified the chemical differences between free and intra-aggregate organic matter, suggesting a modification of soil macro-aggregates dynamics. Interestingly, the four-year climate manipulation affected directly the SOM dynamics, with a decrease in organic C bulk soil content, resulting from significant C-losses in the mineral-associated SOM fraction (MAOM), the most stable form of SOM. This SOC decrease was associated with a decrease in clay content, above- and belowground plants biomass, soil microbial biomass and activity. The combination of these climate changes effects on the plant-soil system could have led to increase C-losses from the MAOM fraction through clay-SOM washing out and DOC leaching in this subalpine grassland.

Keywords: Water extractable organic carbon; Particulate organic matter; Mineral associated organic matter; Infrared spectroscopy; 3D Fluorescence spectroscopy

1. **Introduction**

The fate of soil organic matter (SOM), in terms of accumulation and decomposition is an issue of concern, since a small modification of its global stock may alter the atmospheric greenhouse gas concentration at a decadal timescale (Eglin et al., 2010). Several specific, simultaneously operating, mechanisms in soils can protect SOM from microbial decomposition and thus preserve SOM compounds that would otherwise be rapidly degraded (Leifeld et al., 2009; Sollins et al., 2007; Torn et al., 2009; von Lützow et al., 2006): (i) the selective preservation of recalcitrant materials, a key process during the early phase of the decomposition process (i.e. months to years); (ii) the spatial inaccessibility of SOM compounds (e.g. soil aggregate formation, hydrophobicity of SOM compounds), (iii) the adsorption/co-precipitation of SOM on/by mineral surfaces and (iv) pedoclimatic conditions detrimental to SOM mineralization (e.g., soil frost, low soil pH). Depending on the stabilization mechanisms involved, SOM compounds can remain in soils from days to millennia, and can therefore be roughly classified into SOM pools with contrasting turnover rates (Baisden et al., 2002; Leifeld et al., 2009).

Many physical and/or chemical SOM fractionation methods have been developed to isolate C pools with contrasting turnover rates (von Lützow et al., 2007). The combination of size and density separation is one of the best methods available to obtain such SOM fractions with specific residence times (Sohi et al., 2001; von Lützow et al., 2007) such as: (i) the water extractable organic C (WEOC, <0.45µm); (ii) the free particulate organic matter (freePOM); (iii) the occluded particulate organic matter (occPOM) and (iv) the mineral associated organic matter (MAOM) fractions. The WEOC fraction could be viewed as a readily available resource for microbial communities (Marschner and Kalbitz, 2003). Although soil WEOC only accounts for a few percent of SOC (ca. 0.05-2%, see the review from von Lützow et al., 2007), some components of this fraction cycle extremely rapidly (ca. 4000 times a year,

Boddy et al., 2007) underlining its key functional role in soil. The labile particulate organic matter (POM) fraction consists mainly of weakly decomposed plants debris (Poirier et al., 2005; von Lützow et al., 2007). Particulate SOM fractions could be protected within soil aggregates resulting to a change in its chemistry and its turnover rate. Consequently, the freePOM has a chemistry closer to the one of plant biomass than the occPOM (Helfrich et al., 2006; Kölbl and Kögel-Knabner, 2004; Poirier et al., 2005) and a higher turnover rate (e.g. 6 and 22 years for freePOM compared to 28 and 83 for occPOM according to John et al., 2005 and Baisden et al., 2002). In cold areas, climate and low pH conditions temporarily stabilize these labile POM fractions. The mean turnover rate of the freePOM fraction was recently estimated within the range 80-90 years in various mountain grassland soils (Budge et al., 2011; Leifeld et al., 2009, Meyer et al, 2012a), representing from 20 to 80 % of total C stocks in the first 10 cm of mineral soils (Leifeld and Kögel-Knabner, 2005; Leifeld et al., 2009; Saenger et al., 2015). The mineral associated organic matter (MAOM) fraction represents the passive/slow cycling C pool, with a low turnover rate (142-250 years in Meyer et al, 2011; 534 years in Budge et al, 2011) and a highly microbially processed SOM (low C:N ratio closer to the one of microbial biomass than to the one of plant biomass, and high NMR alkyl-C/O-alkyl-C ratio; Baisden et al., 2002; Budge et al., 2011).

Mountain regions are currently experiencing strong climatic changes altering the temperatures, precipitation and the intensity and duration of seasons. Indeed, shorter periods of snow cover, resulting in longer growing seasons, have been reported to coincide with increasing occurrences of summer droughts and winter freeze-thaw cycles in soils (Gobiet et al., 2014). Such climate changes are likely to alter the C dynamics of mountain soils, from the modification of plant C inputs to the alteration of the various mechanisms of SOM protection from microbial decomposition (Groffman et al., 2001; Davidson and Janssens, 2006; Conant et al, 2011). More specifically, the high C stocks of mountain soils, with high proportions of

freePOM C protected by current cold climate conditions may be highly vulnerable to climate changes (Sjögersten et al., 2011; Torn et al., 2009). Soil moisture conditions are known to alter the WEOC SOM fraction, especially when soil dry conditions are followed by rapid rewetting (Toberman et al., 2008; Zsolnay, 2003). However a marked gap in the understanding of the WEOC fraction dynamics in soils remains (Embacher et al., 2007). The respective amounts of freePOM and occPOM fractions are mediated by C inputs from plants and by the formation/deformation of soil aggregates. Soil aggregation depends on physical processes such as freeze/thaw and dry/rewetting cycles, as well as biological processes such as the activity of soil fauna and plant roots (Six et al., 2004; Davidson et Janssens., 2006; Erktan et al., 2016) that show a strong seasonal pattern in mountain regions and may be altered by climate changes. However the effects of climate modifications on soil aggregation processes and their consequences on the dynamics of SOM fractions have not been studied in great depth (e.g. Cécillon et al., 2010; Conant et al, 2011). The MAOM fraction response to climate change is also highly uncertain and could depend on the type of chemical association of organic C with minerals (Conant et al, 2011). However, the absolute C-losses from this passive/slow cycling C pool under climate changes are expected to be lower than those from the particulate SOM fractions in mountain soils (Sjögersten et al., 2011).

In this study, we investigated the effects of a climate change experiment on the dynamics of SOM pools in subalpine grasslands from the Swiss Jura. We focused on the size and chemistry of four SOM fractions (WEOC, freePOM, occPOM and MAOM fractions) at two sampling dates representing two contrasting seasons: winter and summer. We performed a climate manipulation experiment by transplanting grassland mesocosms along an altitudinal gradient. This four-year climate experiment simulated two climate change scenarios close to current predictions for the 21th century with increased air temperatures ranging between 2 °C

and 4 °C and decreased precipitation ranging between 20 % and 40 % (C2SM, 2011; Frei et al., 2006; Meehl et al., 2007).

We hypothesized that (i) the POM-C fractions (freePOM + occPOM) would represent a large proportion of total SOC in this historically grazed subalpine grassland, especially in the control plots not affected by the climate manipulation ; (ii) the climate manipulation and the strong seasonal climatic changes would affect the quantity and the chemistry of labile SOM fractions (WEOC, free-POM and occPOM). The climate manipulation may affect labile SOM fractions proportionally to their mean turnover rate: WEOC>freePOM>occPOM. (iii) the climate change manipulation would not affect strongly the most stable C pool, stabilized by mineral interactions (MAOM fraction).

2. **Materials and methods**

2.1. Study site, experimental manipulations, and seasonal sampling

The experiment was located in the Swiss Jura mountain range and consisted of a high-to-low elevation soil translocation that, with respect to a disturbance control, simulates a climate warming with an average temperature increase of +2 °C and +4 °C and a precipitation decrease of 20 % and 40 % at the intermediate site and at the lowest the site, respectively. Details about the experimental set-up can be found in Gavazov (2013) and Gavazov (2014a and 2014b). Briefly, in 2009 mesocosm containing turf monoliths of undisturbed soil (30 cm depth) and vegetation, were randomly taken from a mesic grassland grazed by cattle located at 1350 m a.s.l. and transplanted to (i) a control site (1350 m a.s.l., Les Amburnex, N 46°54′, E 6°23′); (ii) an intermediate site (1010 m a.s.l., Saint-George, N 46°52′, E 6°26′) and to (iii) a low-elevation site (570 m a.s.l., Arboretum d'Aubonne, N 46°51′, E 6°37′). Five replicated

156 mesocosms were transplanted per site. The main vegetation consisted of graminoids with few
157 forbs, and the soil could be classified as a Hypereutric Cambisol (IUSS Working Group
158 WRB, 2014) on Jurassic limestone. The aboveground biomass was removed each summer
159 simulating grazing of the pasture to avoid confounding effect of abandonment. During the
160 fourth year of the soil transplantation experiment, two sampling campaigns were performed in
161 winter and summer (February 20th 2013, September 2nd 2013, respectively). Five intact cores
162 of topsoil (5 cm diameter × 10 cm length) per site (one core per mesocosm) were taken at
163 each sampling date (Puissant et al., 2015). Moreover, an additional sampling campaign were
164 performed in summer 2014 to evaluate the soil carbon content along the entire depth of the
165 mesocosm. Five intact soil cores (5 cm diameter × 30 cm length) per site (one core per
166 mesocosm) were taken at the summer 2014 sampling date (Supplementary Fig.S1).
167
168 2.2. Soil microclimate
169 Soil temperature and soil volumetric water content were monitored in all mesocosms over the
170 four-year experimental period (Fig.1). Details of the soil microclimate conditions at the two
171 sampling dates corresponding to winter 2013 and summer 2013 season can be found in
172 Puissant et al. (2015). Briefly, the winter soil temperature was ca. 1 °C at all sites and soil
173 moisture (0-10cm) was ca. 45%. Conversely, soil temperature and moisture showed
174 significant differences between transplantation sites in summer, with a daily mean
175 temperature of 13.2 °C, 16.1 °C, 18.4 °C and a volumetric water content of 33 %, 26 % and
176 21 % for the control, the intermediate and the lowest sites, respectively, for the summer
177 periods of 2009 to 2013. Overall, our climate manipulation increased the mean annual soil
178 temperature by 2 °C and 4 °C (November 2012 to October 2013) at the intermediate (1010m)
179 and at the lowest (570m) sites, respectively. Soil moisture showed a clear decrease throughout
180 the year at the lowest site and a more complex pattern at the intermediate site, depending on

181 the season. Furthermore, the climate manipulation resulted in a longer and warmer plant
182 growing season (with a decrease in snow cover duration) at the intermediate and the lowest
183 sites (Fig.1; Puissant et al., 2015).

184

185 2.3. Basic characterization of bulk soil samples

186 Gravimetric soil water content was measured by drying soil at 105 °C for 48 h according to
187 NF ISO 16586 (2003). For all chemical and texture analyses of bulk topsoils (0-10 cm),
188 samples were dried at 40 °C and sieved (2 mm) following NF ISO 11464 (2006). The particle
189 size distribution (i.e. soil texture) was determined by wet sieving and sedimentation using the
190 Robinson pipette method, according to NF X31-107. Soil pH was measured in H_2O (1:5
191 vol:vol) according to the protocol NF ISO 10390 (2005). Calcareous content was determined
192 following the norm NF ISO 10693 (1995). Soil cations exchange capacity (CEC) was
193 determined according to Metson method described in the protocol NF X 31-130 (1999).
194 Organic C and total nitrogen (N) concentrations were measured by the Dumas dry combustion
195 method after decarbonation (NF ISO 10694, 1995; and 13878, 1995, respectively).

196

197 2.4. Water-extractable organic C fraction

198 To obtain the WEOC fraction, 40 mL of deionized water was added to 10 g of moist sieved (2
199 mm) soil, and shaken for 20 minutes at 250 rpm. Samples were then centrifuged at 10,000 *g*
200 for 10 minutes, after which the solution was filtered through 0.45 mm Millipore filter and
201 immediately stored at -20 °C until analysis. Soil WEOC content was measured using a total
202 organic carbon analyzer (Shimadzu Inc., Kyoto, Japan). The analyzer was calibrated for total
203 dissolved C (TDC) and dissolved inorganic C (DIC) using a calibration solution of potassium
204 hydrogen phthalate ($C_8H_5KO_4$) and a solution containing a mixture of sodium hydrogen

carbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) for TDC and DIC respectively. WEOC was calculated as the difference between TDC and DIC and expressed in mg $C.g^{-1}$ soil.

2.5. Soil organic matter density fractionation

Three SOM fractions (freePOM, OccPOM and MAOM) were separated by density fractionation of oven dried (40 °C) and sieved (< 2 mm) soil samples following Leifeld et al. (2005, 2009). Briefly, 15 g of soil were placed into a 50 mL centrifuge tube. A sodium polytungstate solution (density = 1.6 g cm^{-3}) was added up to the 50 mL line and the tube was gently inverted several times. After 2 hours, floating materials (<1.6 g cm^{-3}) corresponding to the freePOM fraction, were collected and washed thoroughly with deionized water through 0.45 µm nitrocellulose membrane filters. This first step was repeated four times to obtain all remaining freePOM. Then the remaining pellet was re-suspended in sodium polytungstate and treated with ultra-sonication (22 J mL^{-1} in an ice bath using a Branson 250 calibrated according to Schmidt et al (1999) so as to breakdown all soil macro-aggregates (Leifeld and Kögel-Knabner, 2005). After sonication, samples were centrifuged at 10,000 g for 10 minutes and floating materials (occPOM fraction) were collected and washed thoroughly with deionized water through 0.45 µm nitrocellulose membrane filters. This step was repeated four times to collect all occPOM released by the sonication treatment. The remaining pellet corresponding to the MAOM fraction was centrifuged, re-suspended and washed with deionized water through 0.45 µm nitrocellulose membrane filters several times, until obtaining an electrical conductivity < 0.50 mS cm^{-1} (Leifeld and Kögel-Knabner, 2005; Meyer et al., 2012a). We used 0.45 µm nitrocellulose membrane filters so as to characterize the SOC fraction until the WEOC size definition. All washed fractions were oven dried at 40 °C and weighed. Organic C and total N concentrations of the freePOM, occPOM and MAOM fractions were determined using the same methods as for bulk soil samples (see section 2.3).

Organic C and total N concentrations of SOM fractions (expressed as g C or N kg^{-1} SOM fraction) were then expressed as percent of the SOC and total N contents of bulk soil samples (i.e. SOC and total N distribution in SOM fractions).

2.6. Chemistry of the soil organic matter fractions

2.6.1. Chemistry of the WEOC fraction

The chemistry of the WEOC fraction was qualitatively assessed using ultraviolet (UV) spectroscopy. The absorbance of the WEOC fraction at 280 nm was used as an indicator of its aromaticity (Kalbitz et al., 2003). Three dimensions (3D) spectrofluorescence measurements were then performed on the WEOC fraction with a spectrofluorometer (Varian Cary-Eclipse). Placed in a quartz cell (10x10 mm – Hellma Analytics), fluorescence emissions of solutions were recorded between 250 and 500 nm with 5-nm slits (1 nm step) and were excitated in the range from 220 to 310 nm with a step of 15 nm. In order to overcome inner filter effects, solutions were diluted until absorbance at 256 was inferior to 0.01. All data were expressed in Quinine Sulfate Units (Fluorescence data were used to characterise the main fluorophore compounds and their distribution in the WEOC). In order to determine the fluorescent protein-like moieties, emission spectra were simulated by the linear combination of log-normal functions which were shown to simulate organic matter fluorescence (Siano and Metzler, 1969). Simulations were performed by a constraint (for center location and width) least square simulation of a set of user-defined bands (number and positions) using a matlab optimisation toolbox. This method is effective in simulating protein-like fluorophores whose emissions are often masked by Rayleigh or Raman scatterings. The bands were ascribed to Tyrosine-like (λexc/λemi: 235/310), tryptophane-like (235;295 / 350), fulvic-like (235;295;310 /410) and humic-like (295; 310 /480) compounds.

2.6.2. Chemistry of the POM fractions

The chemistry of the POM fractions (freePOM and occPOM) was assessed using mid-infrared (MIR) spectroscopy. Prior to these analyses, POM fractions were ball-milled (< 0.25 mm using a Retsch ZM 200) and further dried overnight at 40 °C to limit interferences with water, without altering OM chemistry. Crushed samples were analyzed using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific Inc., Madison, WI, USA). Spectral acquisition was performed by diamond attenuated total reflectance (MIR-ATR) spectroscopy over the spectral range 4,000–650 cm^{-1}, with spectral resolution of 4 cm^{-1} and 16 scans per replicate (2 replicates per sample). All MIR-ATR spectra were corrected for atmospheric interferences (H_2O and CO_2). Spectral data were further processed and analyzed using the hyperSpec (Beleites and Sergo, 2011), signal (signal developers, 2013) and ptw (Bloemberg et al 2010) packages in the R environment, software version 2.14.0 (R Development Core Team 2011). Five spectral regions corresponding to specific C functional groups were chosen for further characterization (1) the saturated hydrocarbons (SAT) region 2,750–3,025 cm^{-1} corresponding to alkyl C (CH_2, CH_3, and CH); (2) the unsaturated (UNSAT) region 1,700–1,760 cm^{-1} and 1,576–1,618 cm^{-1} corresponding to C=O and aromatic C=C bonds respectively; (3) the polysaccharide (POLY) region 1,222–1,287 cm^{-1} corresponding to O-Alkyl C, and (4) the aromatic CH (AROCH) region 852–898 cm^{-1} (Supplementary Fig.S2) . The contribution of minerals (e.g. phyllosilicates) or polytungstate pollution to the intensities of the five waveband-regions was negligible for these POM fractions. The selected wavebands were used to calculate seven proxies of POM chemistry, according to Pengerud et al (2013) and Robroek et al. (2015): (1) SAT/SOC = hydrophobicity index (SAT = saturated hydrocarbons = Alkyl C, and SOC = soil organic carbon content); (2) C=O/SOC (index of oxidation); (3) C=C/SOC (aromaticity index); (4) MI = C=C/UNSAT (maturation index) (5) POLY/SOC (polysaccharide content); (6) AROCH/C=C (condensation index = degree of condensation of

aromatics), (7) SAT/POLY to estimate the Alkyl-C/Alkyl-O which is used as an indicator of microbial transformation (Budge et al, 2011).

2.7. Statistical analyses

The effect of climate conditions (soil transplantation and sampling dates) and the effect of SOM pools (i.e. SOM fractions) on SOM chemistry (UV and FLUO and MIR-ATR spectroscopy indices), were assessed by three-way mixed effects ANOVAs (Supplementary Table 1). Fixed factors were the sampling date, the transplantation site and the SOM fraction, while the actual mesocosm was added as a random factor and the sampled core (from which the SOM fraction originates) as a nested factor. Data was log or square root transformed when necessary to respect assumptions of normality and homoscedasticity of the residuals. To test the effect of sampling date (season) on each SOM fraction separately, one-way mixed ANOVAs was performed at each transplantation site with the sampling date as fixed factors and the actual mesocosm as a random factor. To test the effect of the climate change experiment (site effect) on each individual variable (SOM fraction, pH, soil moisture, etc.), one-way ANOVA was performed at each season (winter and summer). When significant ANOVAs were obtained at the 5 % error probability threshold, a Tukey's post-hoc test was applied. All statistical analyses were performed under the R environment software 2.14.0 (R Development Core Team 2011), using the R package NLME (Pinheiro et al., 2014).

3. **Results**

3.1. Basic soil characteristics

All soils from the transplanted mesocosms were determined as clay textured soils (USDA texture triangle). An effect of the transplantation on topsoil (0-10 cm) texture was observed,

manifested by a significant decrease in clay content at the intermediate site (clay content = 40.2 % at 1010 m a.s.l.) compared to the control site (clay content = 52.6 % at 1350 m a.s.l.; p-value = 0.02; Table 1). Clay content at the lowest site (at 570 m a.s.l.) was not significantly different from neither the control site nor the intermediate site (clay content = 44.5 %; p-value = 0.12 and 0.52 respectively; Table 1). SOC content of bulk topsoil showed a similar response to the transplantation, with a significant decrease at the intermediate site in winter and at the lowest and intermediate sites in summer (Table 1). This decrease in SOC content induced by the climate change experiment was confirmed at the summer 2014 sampling date. Whatever the depth sampled, the same trend was observed with a decrease in SOC content at the two transplanted site. The difference in SOC content was not significant in 0-5 cm and in 5-10 cm soil layers but were significant for the intermediate site in 10-15 cm soil layer and for both transplanted sites in 15-30 cm soil layer. This result confirmed the decrease in SOC content and showed that the decrease has been accentuated with increasing the soil depth. Surface SOC content showed a strong correlation with clay content ($r = 0.67$, p-value = 0.006). We did not observe any effect of transplantation on soil pH and CEC (Table 1). A seasonal effect on CEC was observed for the lowest site (570 m a.s.l.) with a lower value in summer (Table 1).

3.2. Distribution and chemistry of organic C in SOM fractions

3.2.1. Water extractable organic carbon

Climate manipulation did not impact the WEOC content between the sites (Fig.2). In the two recipient sites (570 and 1010 m) WEOC was lower in winter as compared to summer (Fig.2). Regarding chemistry of organic C in the WEOC fraction, its aromaticity measured by UV absorption at 280 nm was significantly higher in summer than in winter, irrespective of site. This seasonal effect on WEOC chemistry was confirmed by many 3D fluorescence indices.

330 Indeed, WEOC was significantly richer in fulvic-like and humic-like compounds compared to
331 tyrosine-like compounds at the summer sampling date. No seasonal change in
332 tryptophan/humic or tryptophan/fulvic indices was observed (Fig.2). Finally the fluorescence
333 ratio WEOC humic/fulvic increased in summer while the ratio tyrosine/tryptophan increased
334 in winter. We observed a significant decrease in the WEOC tryptophan/fulvic fluorescence
335 ratio (in summer and winter) and in the WEOC tyrosine/fulvic fluorescence ratio (summer
336 only) in the lower altitudinal sites, as compared to the control site (Fig.2).
337
338 3.2.2. SOM density fractions
339 The SOM fractionation scheme used in this study was rather conservative, with an average of
340 only 4.7 % losses of total SOC content when summing the organic C contribution of each
341 density fraction. The mean annual distribution of SOC in SOM fractions showed that most
342 SOC belonged to the MAOM fraction (86 % of SOC content) while freePOM and occPOM
343 comprised 6 % and 8 % of total SOC content respectively. WEOC contribution to SOC was
344 very small (i.e. 0.2%).
345
346 3.2.2.1. Free particulate organic matter (freePOM)
347 Even though the organic C content of the freePOM fraction increased significantly in
348 winter compared to the summer sampling date (significant for the control site; Table 2), its
349 contribution to bulk topsoil was greater at the summer sampling date (10.1%) than at the
350 winter sampling date (1.9%) for all sites, representing ca. 6.9 gC kg^{-1} dry soil in summer and
351 1.2 gC kg^{-1} dry soil in winter (Fig.3). Under the strongest climate change scenario
352 (transplantation site at 570 m a.s.l.) and at the summer sampling date, the freePOM organic C
353 contribution to SOC bulk content was significantly higher than the two other sites (1010 m
354 and 1350 m a.s.l.). The chemistry of the freePOM fraction was not impacted by the climate

manipulation except for the C=O/SOC oxidation index which was significantly lower in winter at the lowest site compared to the control site (Table 2). Conversely, the sampling date (winter vs. summer) strongly affected the chemistry of the freePOM fraction, which was less oxidized (C=O/SOC) and condensed (CI), more aromatic and matured (MI index) in summer than in winter. This significant effect of the sampling date was generally observed at the control site but not at the two other transplantation sites, even if the trend was similar (Table 2). The Alkyl-C/Alkyl-O ratio of the freePOM, which can be used as an indicator of its degree of microbial transformation (Baldock et al., 2007; Budge et al 2011), was consistently higher in winter than in summer despite that this trend was significant only for the intermediate site (1010 m a.s.l).

3.2.2.2. Occluded particulate organic matter (OccPOM)

Contrary to the freePOM, the contribution of the occPOM organic C to the SOC bulk content (5.5 gC kg^{-1} dry soil, i.e. 8%) of topsoils was neither impacted by seasons nor by soil transplantation (climate manipulation; Fig.3). A strong sampling date effect on occPOM organic C content was observed whatever the site considered with a more organic C concentrated occPOM in winter than in summer (Table 2).

The chemistry of the occPOM fraction was not impacted by the climate manipulation. Conversely, we observed a significant effect of the sampling date on the chemistry of the occPOM fraction. The organic C of the occPOM fraction was less humified (HI), had a lower PI index (polysaccharide), and its aromatic C functional groups were less condensed (CI) at the winter sampling date than at the summer sampling date (Table 2). In contrast to the freePOM, the C-alkyl/O-Alkyl ratio of the occPOM fraction was higher at the summer sampling date than at the winter sampling date, even if this trend was significant only for the lowest site (570 m a.s.l.). Moreover, at the summer sampling date the C-alkyl/O-Alkyl ratio

was lower in the freePOM than in the occPOM fraction (significant for the two lowest sites, Table 2). The C/N ratio was higher in freePOM than in occPOM at both sampling dates even if this difference was relatively low and only significant at the summer sampling of the intermediate site (Table 1). We observed an interaction for some IR indices between sites and the chemical differences composition of the fractions. Indeed, the chemical differences between freePOM and occPOM fraction were modulated by the climate change experiment (i.e. site versus fraction effect; Supplementary Table 1).

3.2.2.3. Mineral associated organic matter (MAOM)

We observed a decrease in the MAOM organic C content at the intermediate (1010 m a.s.l., significant in summer and winter) and the lowest site (570 m a.s.l., significant only in summer) compared with the control site (1350 m a.s.l.; Fig.3). The bulk organic chemistry of the MAOM fraction, assessed with the C:N ratio, strongly differed from the chemistry of the freePOM and the occPOM fractions, with a decreasing average C:N ratio from the freePOM (19.3), occPOM (18), to the MAOM (10) fraction. Moreover the SOC content of the MAOM fraction were significantly affected by the climate change manipulation but not by the seasonal change. Indeed, the mean SOC content of the MAOM fraction was significantly lower at the lowest site (59 ± 4 g kg^{-1}, p-value =0.003) and at the intermediate site (52 ± 4 g kg^{-1}, p-value <0.001) compare to the control site (70 ± 2 g kg^{-1}).

4. **Discussion**

The majority of the SOC were found in the MAOM-C fraction with low C:N ratio suggesting a rather high biogeochemical stability (and low turnover rate) of SOC in these mountain grassland soils. The contribution of this biogeochemical stable fraction (MAOM)

405 did not change across seasons contrary to the more labile C-pools (WEOC, C-POM) showing
406 high seasonal changes of their respective contributions to total SOC or/and their chemistry.
407 Surprisingly, the decrease in organic C content for the bulk soil induced by the climate
408 manipulation already observed by Puissant et al. (2015) was not explained by C-losses from
409 fast cycling C-pools (WEOC, freePOM or occPOM), but by significant C-losses in the
410 MAOM fraction after four years of climate change experiment. These findings challenged
411 our three main hypotheses and we discuss below their implications regarding the dynamics of
412 SOC pools in our climate change experiment.

413

414 4.1. Weak contributions of labile SOM fractions to total SOC

415 Contrary to our first hypothesis, the POM-C fractions did not represent a large
416 proportion of total SOC in these mountain grassland soils. This result contrasts with those
417 from other studies on mountain soils which found that a large proportion of total SOC
418 consisted of labile POM fractions (Budge et al., 2011; Leifeld et al., 2009; Martinsen et al.,
419 2011; Saenger et al., 2015). Indeed, Martinsen et al. (2011) reported that the POM fraction
420 contained more than 60% of total SOC in the first 5 cm of a low-alpine (1050-1320 m a.s.l.)
421 grasslands soil (with or without sheep grazing) from southern Norway. Similar results were
422 reported by Leifeld et al (2009) in the uppermost layers of high altitude (2200 m a.s.l.)
423 permanent mountain grasslands with more than 80% of total SOC contained in the POM
424 fraction. Saenger et al (2015) recently reported that 38 % of total SOC was found in the POM
425 fraction in a French mesic grassland on limestone at 1567 m a.s.l. grazed by sheep. By
426 combining several studies of Swiss mountain grasslands ranging in altitude from 1210 to
427 1410 m a.s.l. (i.e. similar to the studied grasslands in the Jura mountains), Leifeld et al (2009)
428 reported that the proportion of C-POM in the first 10 cm of soils ranged from ca. 24 to 27 %.

These latter results are closer to our findings. Leifeld and Kögel-Knabner (2005) and Meyer et al (2012b) have shown that the land use and the management type could impact the relative proportion of SOM fractions. Here the pasture management (grazing by cattle and then mown during the four years experiment) could partly explain the low proportion of POM-C in these mountain subalpine soils, with large parts of the herbaceous biomass taken up by grazing. Such effect of grazing on POM-C has already been reported (Martinsen et al, 2011, but see Leifeld and Fuhrer, 2009; Meyer et al 2012b). Overall, our results and those from the literature suggest that altitude and grazing may interact to control the POM-C content of mountain subalpine topsoils. The WEOC fraction yielded the smallest contribution to SOC (0.09 to 0.34 %) and this result was consistent to other studies using similar methodologies (see e.g. Rees and Parker, 2005). In this study, SOM consisted mostly of MAOM which has achieved a higher degree of microbial transformation as attested by its low C:N ratio as compared to the freePOM and occPOM fractions. A decrease in C:N ratio from labile (POM) to the MAOM fraction is generally found (Budge et al, 2011;Golchin et al, 1994 ; Baisden et al, 2002). High amounts of MAOM-C with low C:N ratio suggest a rather high biogeochemical stability (and low turnover rate) of SOC in these mountain grassland soils, which contrasts with current knowledge presenting mountain soils as huge reservoirs of labile C (Sjögersten et al., 2011; Leifeld et al., 2009; Saenger et al., 2015).

4.2. Weak impact of the climate change experiment on the labile SOM fractions and their seasonal dynamics

4.2.1. Seasonal dynamics of the labile SOM fractions

As we hypothesized, the strong seasonal climatic changes characterized by a winter period with a continuous snow cover at all sites, and a warm and relatively dry summer

affected the dynamics of the most labile SOM fractions. Only the occPOM fraction contribution was not affected by the seasonal change.

The WEOC fraction considered as the most available substrate for microorganisms was very sensitive to seasonal climatic variations. Both, WEOC abundance and chemistry were strongly impacted by seasonal changes. We observed globally higher WEOC contents in the summer season combined with a more recalcitrant WEOC chemistry (higher UV absorbance at 280nm and higher proportion of aromatic C, fulvic and humic C compared to proteic C). Such temporal dynamics of WEOC content has been previously observed, with higher WEOC content (Yano et al., 2000; Kaiser et al., 2001) and higher humic chemistry in the summer season (Kaiser et al 2001, Qualls and Haines, 1992). However studies specifically characterising the seasonal pattern of WEOC chemistry are few, and contradictory patterns have also been reported (see the review by (Embacher et al., 2007). Our study identifies that this seasonal pattern of WEOC abundance were decoupled from soil microbial abundance and activity (Puissant et al, 2015). This contrasts with several other studies showing positive correlations (Marschner and Bredow, 2002; Marschner and Kalbitz, 2003; Rees and Parker, 2005) and could indicate that WEOC abundance may not be the limiting factor for microbial growth which is more affected by summer drought in these subalpine grasslands.

The freePOM fraction also showed an important seasonal pattern with a higher contribution to total SOC at the summer sampling date. This result could be linked to the seasonal root dynamics which is a significant component of soil C inputs in grasslands (Gregorich et al., 2006; Hitz et al., 2001). Contrary to the freePOM fractions, the relative contribution of the occPOM fraction to total SOC did not show any seasonal trend, underlining its different biogeochemical reactivity compared to the freePOM fraction, as previously reported by Meyer et al. (2011). Interestingly, the organic chemistry of the freePOM and the occPOM fractions (mid-infrared spectroscopic proxies) showed a seasonal

478 pattern, as well as chemical differences between both POM-C fractions. Our results suggest
479 that fresh OM inputs (low Alkyl-C/Alkyl-O ratio) are incorporated into the freePOM fraction
480 during summer. In winter, elements of the freePOM are incorporated into the occPOM
481 fraction (lower Alkyl-C/Alkyl-O ratio in winter compared with summer for the occPOM
482 fraction). The seasonal difference in the chemistry of the occPOM fraction underlines the
483 ontogeny of plant detritus during the aggregation process on a seasonal timescale (Cécillon et
484 al., 2010; Moore et al., 2004).

485 4.2.2. Evolution of the labile SOM fractions induced by the climate manipulation

486 Contrary to our second hypothesis, the climate change manipulation did not strongly
487 affect the respective contributions of labile SOC pools (WEOC, freePOM and occPOM) to
488 total SOC. The only labile SOM fraction impacted by the climate manipulation experiment
489 was the freePOM fraction. A minor increase in the relative contribution of freePOM-C to total
490 SOC was observed at the lowest site (570m, only significant at the summer sampling date).
491 Here, the freePOM fraction could accumulate under climate manipulated conditions because
492 of the decreased microbial activity (enzyme pools and soil respiration) observed on the same
493 plots, probably due to the effect of water limitation at lower transplantation sites (Mills et al.,
494 2014; Puissant et al, 2015; Gavazov et al, 2014a). As a consequence, the effect of the climate
495 manipulation on the contribution of the labile SOM fractions (small increased contribution of
496 freePOM-C to total SOC) could not explain the overall losses in bulk SOC observed after four
497 years of experiment. Interestingly, the chemical differences between the freePOM and the
498 occPOM fractions were modulated by the climate manipulation (Supplementary Table 1),
499 suggesting a climate change induced modification of soil macro-aggregates dynamics. Other
500 studies have shown that physical occlusion of OM within soil aggregates could be affected by
501 the climate conditions like freeze-thaw cycles (Sollins et al., 1996). The modification of soil

502 macro-aggregates dynamics under climate change could have potentially important
503 repercussions on the long term soil C dynamics.

504

505 ### 4.3. Large C-losses from the MAOM fraction under the climate change
506 manipulation

507 Contrary to our third hypothesis, significant C-losses from the MAOM fraction, the most
508 biogeochemically stable fraction, were observed after four years of climate change
509 manipulation. These C-losses coincided with the decrease in organic C content for the bulk
510 soil already observed in the same experiment (Puissant et al, 2015) in the topsoil, which was
511 even more pronounced at greater soil depth (10-15 cm and 15-30 cm; Fig.S1). This climate-
512 induced modification on MAOM-C content was also linked to an important textural change,
513 with a decrease in clay content at the lower transplantation sites.

514 In order to understand this climate-induced modification of SOC content, it is necessary to
515 frame the observed SOM dynamics in an ecosystem context, considering both soil C inputs
516 and outputs. Previous investigations of the same soil transplantation experiment revealed the
517 following effects of the climate manipulation on SOM dynamics: (i) a significant decrease in
518 SOM outputs through respiration (Mills et al., 2014), which was confirmed by a decrease in
519 soil enzyme pools and soil microbial biomass (Puissant et al, 2015); (ii) an increase in SOM
520 outputs through dissolved organic matter leaching (+ 9.9 mg C L^{-1} at the lowest site and + 4.2
521 mg C L^{-1} at the intermediate site relative to high elevation controls; Gavazov, 2013); (iii)
522 irregular changes of aboveground SOM inputs (aboveground biomass production) depending
523 on the year (Table 3); (iv) a strong decrease in belowground SOM inputs through a huge
524 decrease of root biomass (Table 3).

In combination with these results, our present study illustrates that climate-manipulation caused C losses through a reduction in belowground plant C inputs together with enhanced leaching processes. The intense C-leaching may itself be linked to several observed changes of soil parameters under the climate manipulation. Indeed, decreased root biomass and microbial biomass and activity could have resulted in changes of soil structure and its resistance to climate events such as precipitation events. Root biomass has been shown to be an important factor controlling soil erosion and leaching (Gyssel et al, 2005). Moreover, the microbial products of decomposition, reduced under the climate manipulation, are the main precursors of stable SOM by promoting SOM formation, aggregation and association to mineral matrix (Cotrufo et al, 2013, Malik et al, 2016). The observed modification of soil macro-aggregates dynamics under climate change further coincide with this hypothesis. In fact, such changes in soil structure could have increased clay dispersion which has then led to a vertical migration of clay colloids down the mesocosms.

The important MAOM-C losses following the climate change manipulation may thus be explained by washing out of clay-SOM associations leading to the strong difference in soil texture and the increase in C-leaching observed (Gavazov, 2013). Losses of organic C through leaching has been shown to be an important factor within the C cycle of grasslands (5 to 98 % of C net ecosystem exchange; Kindler et al., 2011). However in our study, losses of clays and associated MAOM-C following the climate change manipulation may have been artificially enhanced by the use of mesocosms of 30 cm depth. In real grassland ecosystems, migration of clay colloids and C-leaching could be stabilized at a greater soil depth, but it is likely that some of the destabilized clay-SOM associations would be lost.

Conclusion

Our study shows that most of the SOC content of these subalpine grazed grassland soils was contained in the stable MAOM fraction. As expected, the most labile C pools (WEOC and freePOM) showed a high intra-annual dynamics (amounts and chemistry) mediated via the seasonal changes of fresh plant debris inputs and confirming their high contribution to the microbial loop. The amount of OM occluded into soil macro-aggregates was constant between seasons and sites, whereas its chemistry changed. Such results confirmed the relatively short turnover time of soil macro-aggregates and suggest an effect of the climate change manipulation on soil macro-aggregate dynamics. Four years of reduced precipitation and higher mean annual temperature led to a decrease of total SOC concentration due to a decrease of SOC content in the MAOM fraction. The combined effects of the reduction in plants inputs, roots biomass, microbial biomass and activity could have led to change the soil structure and its resistance to climate events. The decrease in clay content and the increase in DOC leaching under climate change manipulation support the hypothesis of C-losses form MAOM fraction through clay-SOM washing out and DOC leaching in this subalpine grassland. We ask for more studies to understand possible environmental cascade reactions impacting the soil carbon cycle under a warming world. Our results highlight the importance of (i) quantifying the seasonal dynamics of labile SOM pools and (ii) considering SOM outputs linked with processes such as erosion or C-leaching so as to understand the fate of soil carbon change under climate change.

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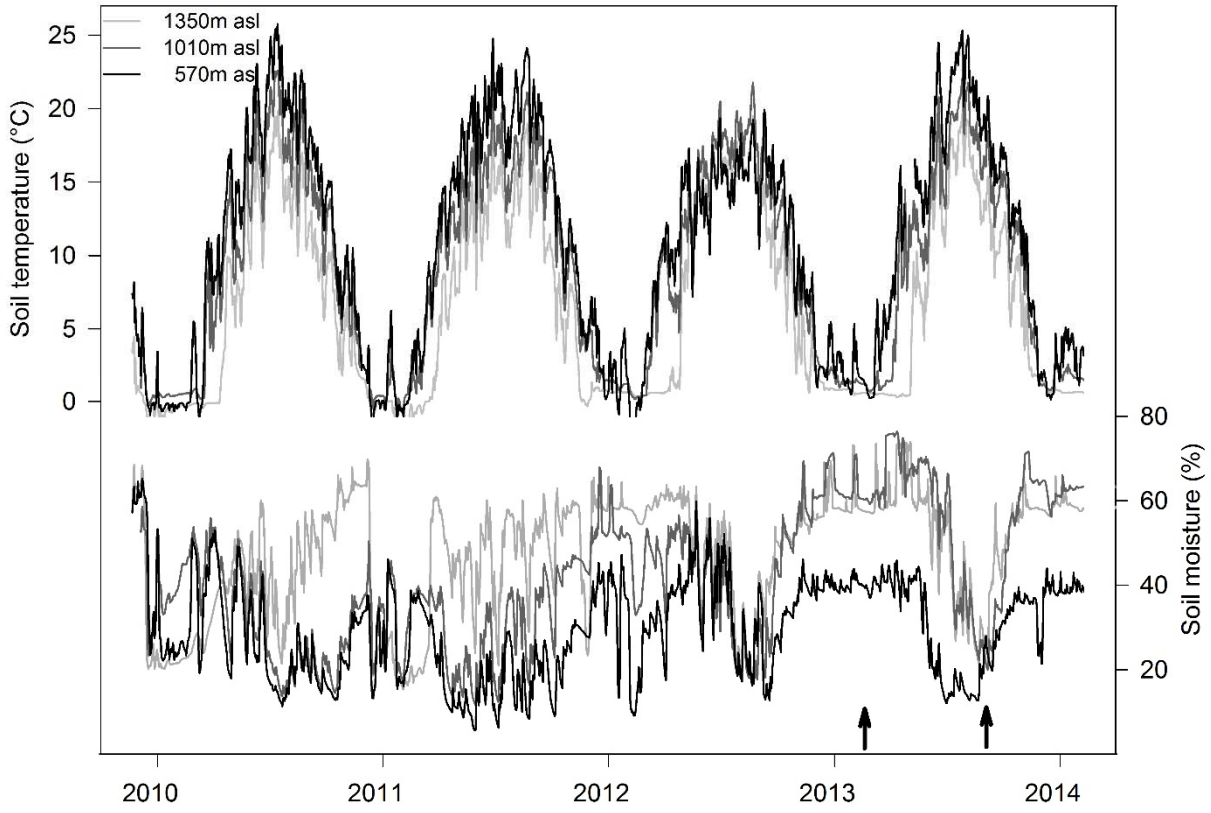

Fig.1. Daily mean soil temperature and moisture of soil mesocosms at each site from the beginning of the experiment (2009) to the year 2014. Control site (1350 m a.s.l.) in light grey line intermediate site (1010 m a.s.l.) in grey line; lowest site (570 m a.s.l.) in dark line. The two black arrows indicate the winter and summer dates of soil sampling in 2013.

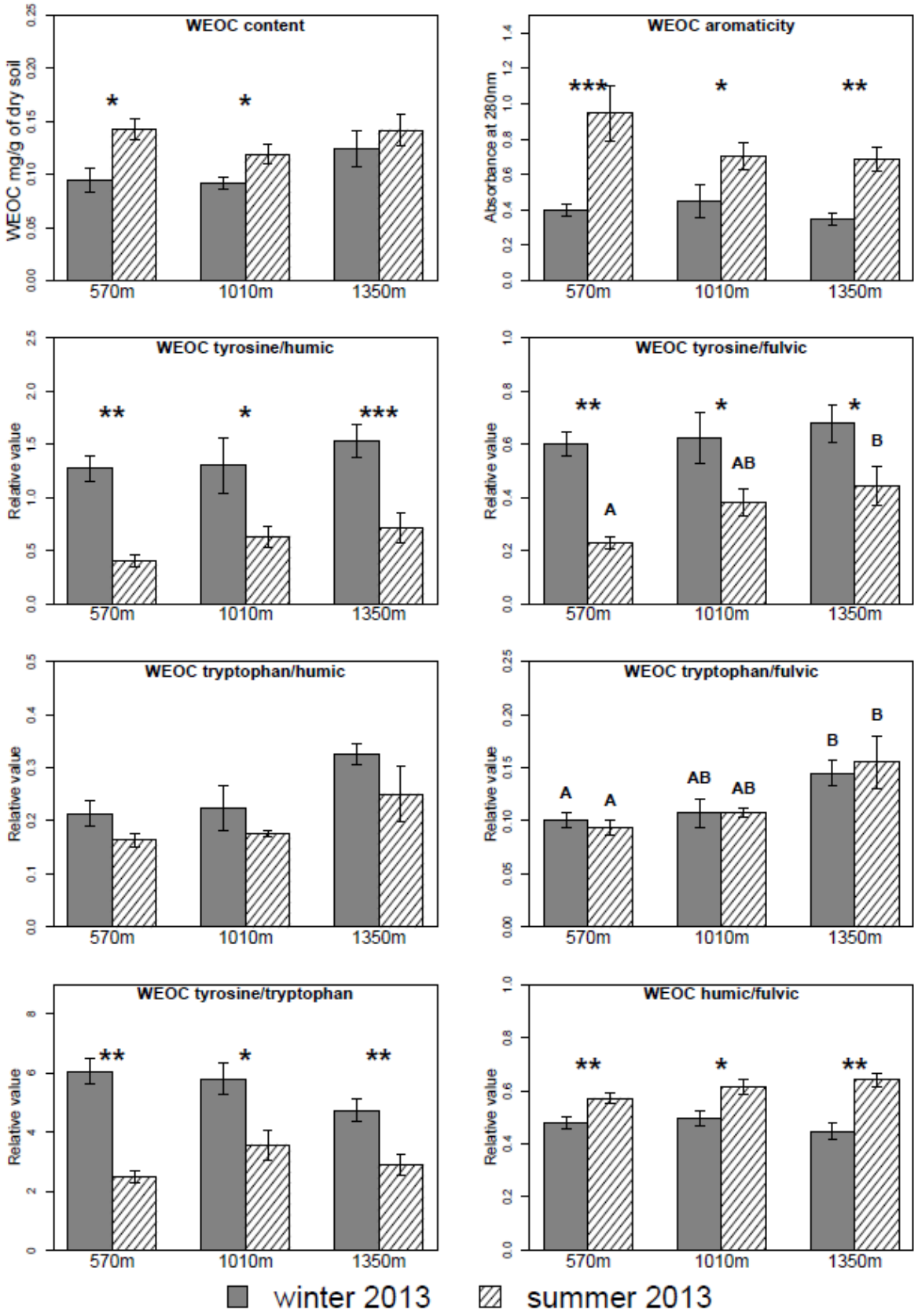
WEOC content
WEOC mg/g of dry soil
0.00
0.05
0.10
0.15
0.20
0.25
*
*
570m
1010m
1350m
WEOC aromaticity
Absorbance at 280nm
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
***
*
**
570m
1010m
1350m
WEOC tyrosine/humic
Relative value
0.0
0.5
1.0
1.5
2.0
2.5
**
*
***
570m
1010m
1350m
WEOC tyrosine/fulvic
Relative value
0.0
0.2
0.4
0.6
0.8
1.0
**
*
*
A
AB
B
570m
1010m
1350m
WEOC tryptophan/humic
Relative value
0.0
0.1
0.2
0.3
0.4
0.5
570m
1010m
1350m
WEOC tryptophan/fulvic
Relative value
0.00
0.05
0.10
0.15
0.20
0.25
A
A
AB
AB
B
B
570m
1010m
1350m
WEOC tyrosine/tryptophan
Relative value
0
2
4
6
8
**
*
**
570m
1010m
1350m
WEOC humic/fulvic
Relative value
0.0
0.2
0.4
0.6
0.8
1.0
**
*
**
570m
1010m
1350m
winter 2013
summer 2013

Fig.2. Water extractable organic carbon (WEOC) abundance and chemistry (UV absorbance and fluorescence). Protein-like fluorophores for tyrosine, tryptophane, fulvic and humic compounds were simulated (see methods). Control site (1350 m a.s.l.); intermediate recipient site (1010 m a.s.l.); lowest recipient site (570 m a.s.l.). Asterisk symbols indicate significant differences between winter and summer season at each site (* for $p<0.05$, ** for $p<0.01$; *** for $p<0.001$). Uppercase letters indicate significant differences between transplantation sites (climate manipulation) at each sampling date (season) ($p<0.05$, climate manipulation effect)

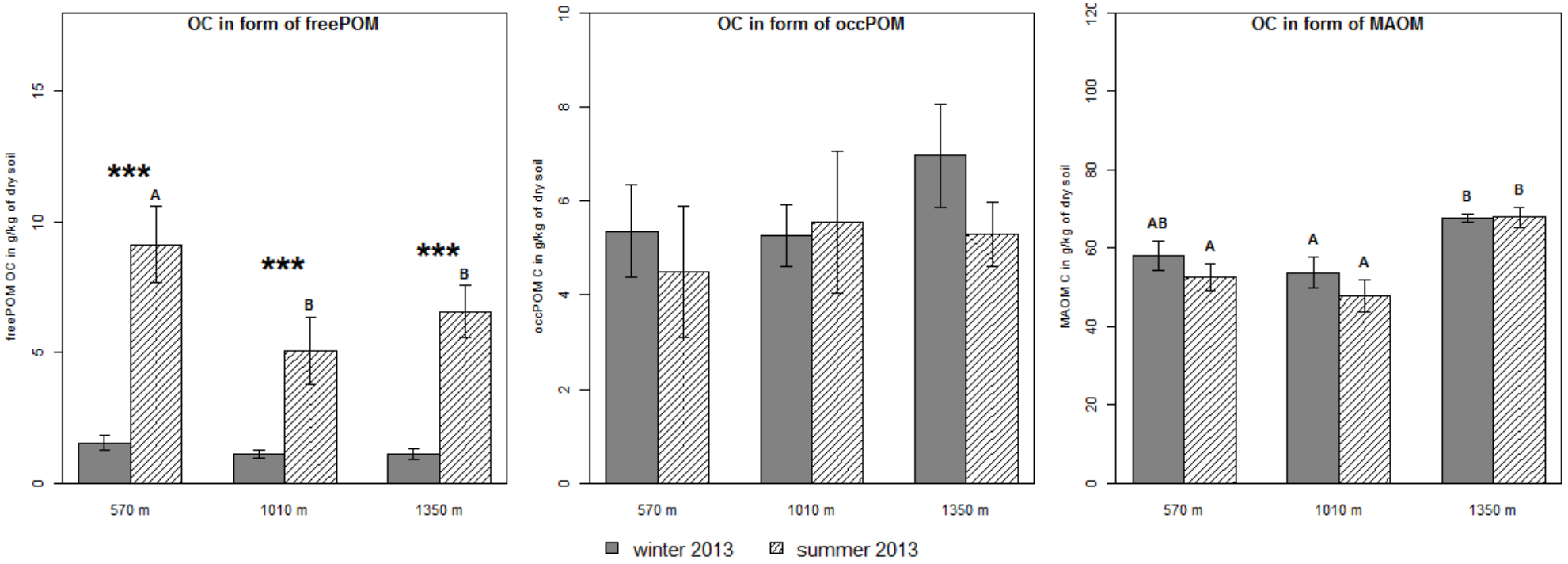

Fig.3. Contribution of freePOM, occPOM and MAOM SOC fractions to bulk soil (gC / kg dry bulk soil). Control site (1350 m a.s.l.); intermediate site (1010 m a.s.l.); lowest site (570 m a.s.l.). Post hoc HSD tests are represented with different bold letters to indicate significant differences ($p<0.05$). Uppercase letters indicate significant differences between transplantation sites for each sampling date (winter or summer). Asterisk symbols indicate significant differences between winter and summer season at each site (* for $p<0.05$, ** for $p<0.01$; *** for $p<0.001$)

Sampling dates		Winter (February 20th, 2013)			Summer (September 2nd, 2013)		
Site	**m a.s.l.**	**570**	**1010**	**1350**	**570**	**1010**	**1350**
Soil moisture	**%**	**43 ± 2*A***	**44 ± 2*A***	**50 ± 2*A***	**21 ± 1*B a***	**26 ± 2*B a***	**33 ± 1*B b***
Soil temperature	**^{0}C**	**1,2 ± 0,4*A***	**1,2 ± 0,2*A***	**0,6 ± 0,2*A***	**18,4 ± 0,4*B a***	**16,1 ± 0,1*B b***	**13,2 ± 0,2*B c***
pH	**-**	**5,7 ± 0,2*A***	5,9 ± 0,2	5,7 ± 0	**5,4 ± 0,2*B***	5,7 ± 0,2	5,6 ± 0,1
Calcareous	**g.kg^{-1}**	2,6 ± 0,2	2,2 ± 0,2	2,2 ± 0,4	3,6 ± 1,1	2,4 ± 0,2	1,8 ± 0,2
CEC	**cmol.kg^{-1}**	**33,9 ± 3,7A**	32,2 ± 4,5	38,4 ± 1,5	**26,2 ± 2,3B**	29 ± 4	36,6 ± 1,7
SOC	**g.kg^{-1}**	**66,5 ± 4,3ab**	**60,7 ± 4,6b**	**77,5 ± 2,1a**	**69,8 ± 6,7a**	**57,2 ± 5,3a**	**81,1 ± 4,1b**
Soil total nitrogen	**g.kg^{-1}**	**6,1 ± 0,4ab**	**5,7 ± 0,5a**	**7,4 ± 0,2b**	**5,8 ± 0,4a**	**5,2 ± 0,5a**	**7,5 ± 0,4b**
C/N		10,8 ± 0,2	10,7 ± 0,2	10,5 ± 0,1	12 ± 0,8	10,9 ± 0,2	10,8 ± 0,1
Clay	**g.kg^{-1}**		-		**445 ± 40*ab***	**402 ± 22*a***	**526 ± 9*b***
Silt	**g.kg^{-1}**		-		280 ± 16	283 ± 14	291 ± 6
Sand	**g.kg^{-1}**		-		275 ± 56	315 ± 30	182 ± 10

Table 1: Basic soil characteristics for winter and summer sampling dates in the experimental sites. The highest elevated site (1350 m a.s.l.) corresponds to the control site, and the two sites at 1010 and 570 m a.s.l. to the transplanted recipient sites. Values represent the mean (n=5) with the associated standard error (SE). Post hoc HSD tests are only represented with different bold letters to indicate significant differences ($p<0.05$). Uppercase letters indicate significant differences between sampling dates (winter/summer) at each site. Lowercase letters indicate significant differences between sites (manipulation effect) at each sampling date.

Sampling dates	Winter (February 20th 2013)			Summer (September 2nd 2013)		
Site (meters)	**570**	**1010**	**1350**	**570**	**1010**	**1350**
OC content (g.kg of dry fraction)						
free POM	**267 ± 14a**	285 ± 15	**309 ± 14A**	243 ± 11	256 ± 6	**256 ± 4B**
occluded POM	**329 ± 6b A**	**294 ± 8A**	**307 ± 8A**	**258 ± 3B**	**247 ± 18B**	**231 ± 11B**
C/N						
free POM	19 ± 1a	19 ± 2a	19 ± 1a	19 ± 1a	**20 ± 1a**	19 ± 1a
occluded POM	18 ± 0a	18 ± 1a	18 ± 0a	17 ± 0a	**18 ± 1b**	18 ± 0a
MAOM	**10 ± 0c**	**10 ± 0c**	**10 ± 0c**	**10 ± 0c**	**10 ± 0c**	**10 ± 0c**
HI index (humification)						
free POM	6.1 ± 0.2	6.5 ± 1	7 ± 0.6	**5.4 ± 0.3a**	**6.2 ± 0.5a**	5.7 ± 0.2
occluded POM	6 ± 0.3	**6.1 ± 0.6A**	5.6 ± 0.6	**8.1 ± 0.9b**	**8.7 ± 0.8b B**	7 ± 0.5
C=O/SOC (oxidation)						
free POM	**9.8 ± 0.9A α**	**12.8 ± 2.9a αβ**	**18.8 ± 2.7a A β**	**4.7 ± 0.9B**	7.6 ± 1.6	**7.4 ± 0.6B**
occluded POM	7.3 ± 0.9	**6.1 ± 0.7b**	**5.9 ± 1.2b**	6.8 ± 1	7.4 ± 1.1	5.9 ± 0.7
C=C/SOC (aromaticity)						
free POM	3.3 ± 0.4	2.7 ± 0.6	**1.7 ± 0.6A**	3.3 ± 0.2	3.5 ± 0.5	**3.9 ± 0.2B**
occluded POM	3.1 ± 0.3	2.9 ± 0.3	**3.9 ± 0.3b**	3 ± 0.4	3.2 ± 0.7	3.6 ± 0.2
MI Index (maturation)						
free POM	2.5 ± 0.4	**2.1 ± 0.6a**	**1 ± 0.5aA**	4.3 ± 0.7	3.3 ± 0.6	**3.5 ± 0.2B**
occluded POM	3 ± 0.4	**3.3 ± 0.5b**	**4.2 ± 0.5b**	3.2 ± 0.6	3.1 ± 0.8	3.9 ± 0.5
PI index (polysaccharide content)						
free POM	8.5 ± 0.4	7.6 ± 0.7	9.8 ± 0.8	8 ± 0.2	9.5 ± 0.9	9.5 ± 0.3
occluded POM	8.2 ± 0.3	8 ± 0.7	**8.1 ± 0.6A**	8.5 ± 0.4	9.5 ± 0.6	**10 ± 0.6B**
CI Index (condensation)						
free POM	6.3 ± 1.5	10.9 ± 4.6	**15.6 ± 3.1a A**	**3.3 ± 0.7a**	**6 ± 0.9a**	**4.1 ± 0.5a B**
occluded POM	**2.5 ± 0.8A**	**5 ± 1.4A**	**3.1 ± 0.8b A**	**12 ± 1.6b B**	**18.5 ± 5.9b B**	**13.6 ± 2.8b B**
Alkyl-C/Alkyl-O (microbial transformation)						
free POM	7.2± 0.7	**7.6 ± 0.1A**	7.1± 0.2	**6.7 ± 0.4a**	**6.6 ± 0.4a B**	6 ± 0.2
occluded POM	**7.3 ± 0.3A**	7.6 ± 0.1	6.9 ± 0.4	**9.6 ± 1.2b B**	**9.2 ± 1.2b**	7 ± 0.3

Table 2: Chemical characteristics of freePOM, occPOM and MAOM fractions of SOC. Organic content of the fractions expressed in g Kg^{-1} of SOC, CN ratios and proxies of POM bulk chemistry calculated from MIR analysis are given. Mean values (n=5) with the associated standard error (SE) are given. Post hoc HSD tests are represented with different bold letters to indicate significant differences ($p<0.05$). Uppercase letters indicate significant differences between sampling dates (winter/summer) at each site and for each fraction. Lowercase letters indicate significant differences between fractions at each sampling date and site. Greek letters indicate significant differences between transplantation sites

Sampling year	Biomass	Unity	Site			Comparison to control site (%)		Reference
			1350 m	1010 m	570 m	1010 m	570 m	
2010	Aboveground	*g.m²*	416	375	295	-10	-29	Gavazov et al., 2013
2011			250	240	95	-4	-62	Gavazov et al., 2014b
2012			233	368	414	58	78	Gavazov 2013
2014			426	561	505	32	19	*unpublished*
2014	Belowground		1890	967	751	-49	-60	*unpublished*

Table 3: Mean aboveground and belowground biomass ($g.m^2$) per year at each transplanted site.

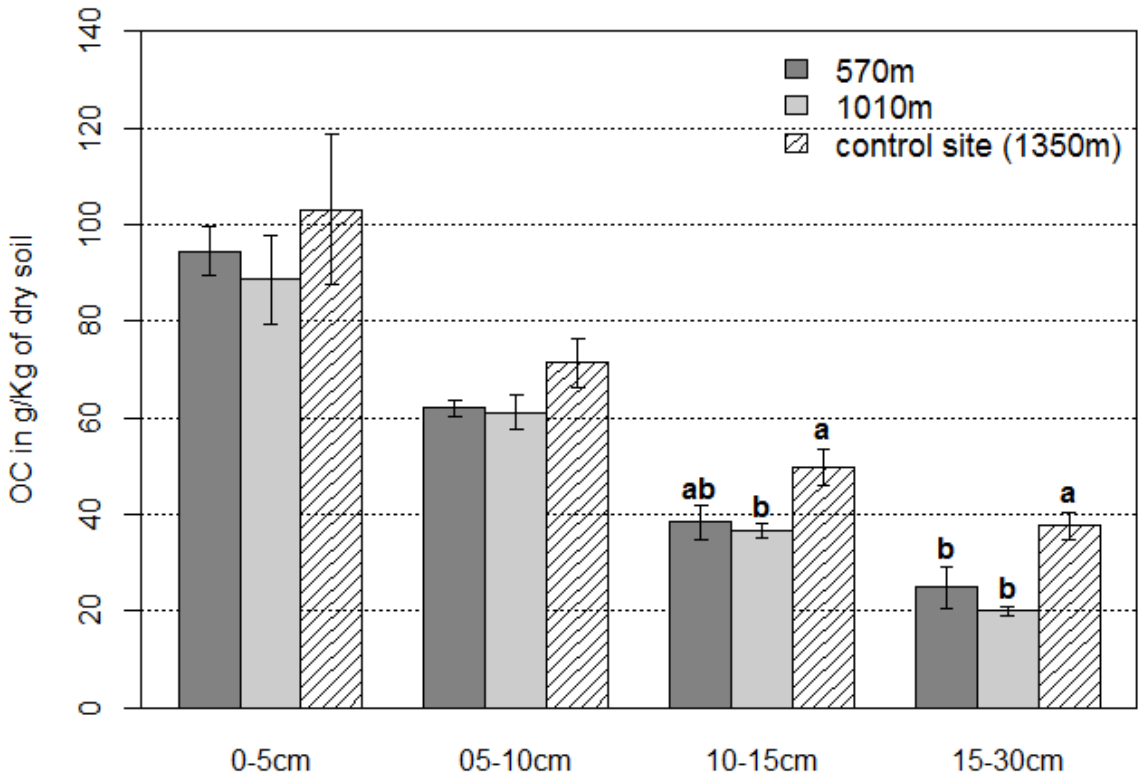

Figure S1. Soil organic carbon content for the four soil depths sampled in summer 2014. Error bars represent the standard errors of the mean values (n = 5). Lower case letters indicate significant differences between transplantation sites (climate manipulation) at each soil depth.

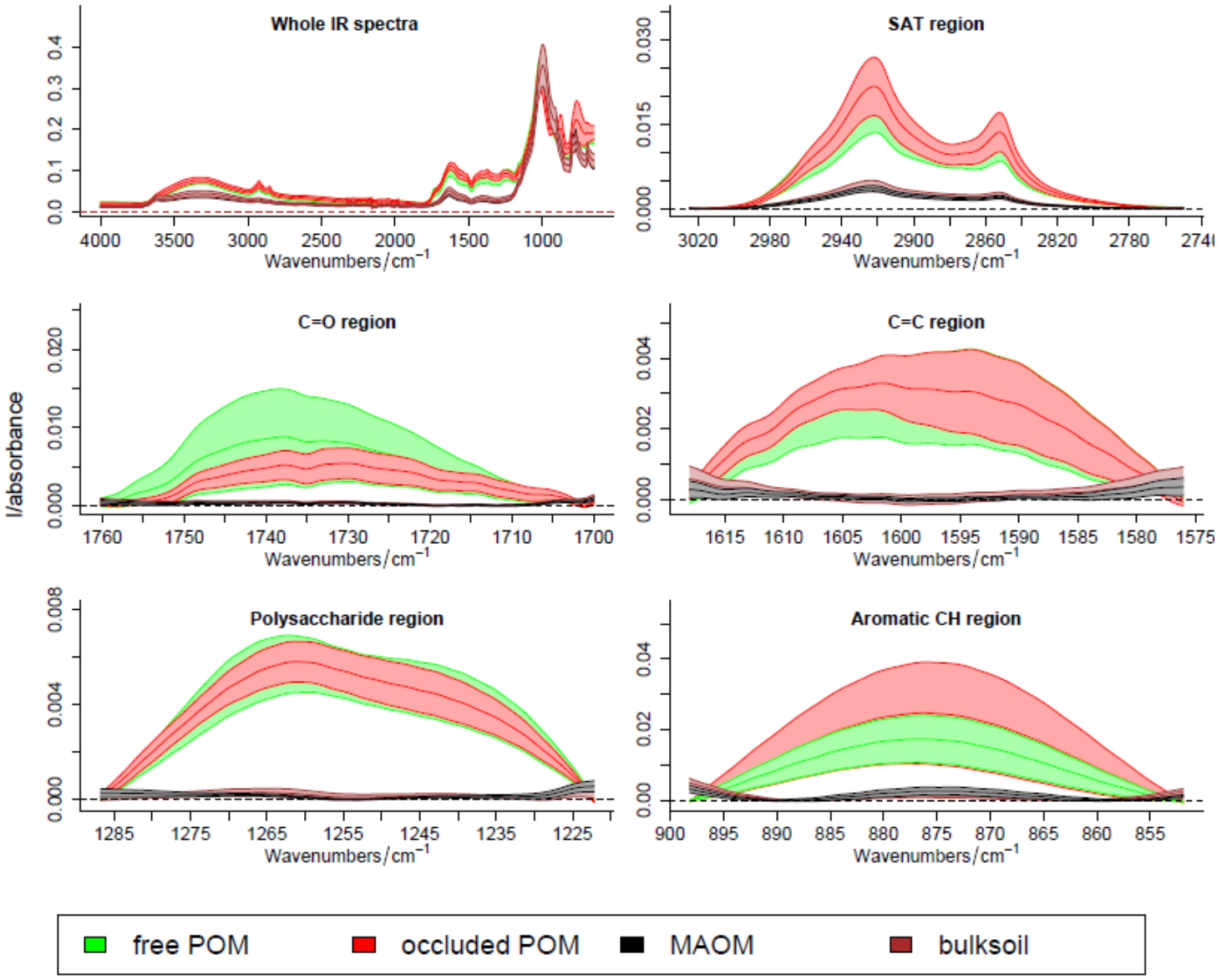

Figure S2. Spectral regions of mid-infrared spectroscopy selected for building specific C functional indices. The whole spectra chart indicates a highly different IR signal between POM fractions (free and occluded) and both MAOM fraction and bulk soil.

	season		site		fraction		season:site		season:fraction		site:fraction	
Mixed models F and P values	**F**	**P**	**F**	**P**	**F**	**P**	**F**	**P**	**F**	**P**	**F**	**P**
IR indices (freePOM and occPOM)												
HI	3.96	0.07	0.43	0.66	5.15	*	0.77	0.49	20.50	***	1.92	0.17
C=O/SOC	19.38	***	0.59	0.57	22.93	***	1.49	0.26	28.26	***	9.64	***
C=C/SOC	3.89	0.07	0.08	0.92	2.46	0.13	1.45	0.27	13.98	**	7.35	**
MI	12.54	**	0.12	0.89	12.54	**	0.62	0.55	25.27	***	10.39	***
PI	9.63	**	1.58	0.25	0.21	0.65	3.67	0.06	2.83	0.11	0.87	0.43
CI	7.43	*	1.66	0.23	0.05	0.83	0.93	0.42	48.55	***	0.91	0.42
Alkyl-C/Alkyl-O	0.07	0.78	3.33	0.07	15.95	***	2.76	0.08	29.13	***	1.53	0.23
3D fluorescence indices (WEOC)												
Tyrosine/Humic	94.70	***	1.64	0.24	---	---	2.28	0.14	---	---	---	---
Tyrosine /Fulvic	49.70	***	3.03	0.09	---	---	3.49	0.07	---	---	---	---
Tryptophane/ Humic	7.90	*	6.00	*	---	---	0.20	0.80	---	---	---	---
Tryptophane / Fulvic	0.00	0.99	11.03	**	---	---	0.24	0.79	---	---	---	---
Tyrosine / Tryptophane	76.14	***	1.80	0.20	---	---	3.20	0.07	---	---	---	---
Humic / Fulvic	70.03	***	0.30	0.74	---	---	3.54	0.06	---	---	---	---

Supplementary Table 1: Effects of sampling date, climate manipulation, fraction and interactions of these three factors on C-POM and WEOC bulk chemistry. Definition of the IR indices: (1) SAT/SOC = hydrophobicity index (SAT = saturated hydrocarbons = Alkyl C, and SOC = soil organic carbon content); (2) C=O/SOC (index of oxidation);

(3) C=C/SOC (aromaticity index); (4) MI = C=C/UNSAT (maturation index) (5) POLY/SOC (polysaccharide content); (6) AROCH/C=C (condensation index = degree of condensation of aromatics), (7) SAT/POLY to estimate the Alkyl-C/Alkyl-O. Definition of the 3D Fluorescence indices: Tyrosine-like (λexc/λemi: 235/310), tryptophane-like (235;295 / 350), fulvic-like (235;295;310 /410) and humic-like (295; 310 /480) compounds. *Significance codes for ANOVA's are (***) $p<0.001$; (**) $p<0.01$; (*) $p<0.05$.*