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Abstract

In a future warmer world, peatlands may change from a carbon sink function to a carbon source function. This study tracks changes in water-extractable organic matter (WEOM) after one year of *in situ* experimental warming using open-top chambers (OTCs). WEOM was studied in the upper peat layers (0-10 cm) through analysis of water-extractable organic carbon (WEOC), stable C isotopic composition ($\delta^{13}C$), specific UV absorbance at 280 nm and sugar composition of peat cores taken from an open bog (DRY sites) and a transitional poor fen (WET sites).

At the DRY sites, the impact of OTCs was weak with respect to WEOM parameters, whereas at the WET sites, the air warming treatment led to a decrease in peat water content, suggesting that the supply of heat by OTC's was used mainly for evapotranspiration. OTCs

at the WET sites also induced a relative enrichment at the surface (0 to 5 cm depth) of aliphatic and/or aromatic compounds with concomitant decrease of WEOC, as a result of decomposition. On the contrary, WEOC and sugar contents increased in the deeper peat layer (7.5–10 cm depth) probably as a result of increased leaching of phenolic compounds by roots, which then inhibits microbial activities.

The different responses to experimental warming at DRY and WET sites suggest that the spatial variability of moisture in the peatland is critical for the understanding of the impact of global warming on the fate of organic matter and the carbon cycle in peatlands.

Key words: carbohydrates; climate change; organic matter; $SUVA_{280}$; OTC; carbon isotope

1. Introduction

Owing to an imbalance between primary production and organic matter (OM) decay, northern peatlands - which contain about 455 Pg carbon (C) - currently act as an important C sink (Clymo, 1983; Gorham, 1991). The peatland sink function is mainly due to interactions of several factors such as water logging, anoxia, acidity and low temperature, which limit OM decomposition (Moore and Knowles, 1990; Laiho, 2006). Peatlands are predominantly abundant in continental boreal and sub-boreal regions where a greater temperature increase is expected over the next century (Immirzi and Maltby, 1992; IPCC, 2007). If environmental constraints which favour C sequestration change (Davidson and Janssens, 2006), peatlands may switch from a C sink to a C source function (Oechel et al., 1995; Waddington and Roulet, 1996).

To determine the response of peatland ecosystems to climate change, *in situ* warming experiments are now commonly performed, e.g. with open-top chambers (OTCs). Up to now, most studies on the impact of OTCs on peatland functioning dealt with changes in plant communities and primary production (Dorrepaal et al., 2004; Aerts et al., 2006; Sullivan et al., 2008) or with CO_2-CH_4 balance (Welker et al., 2004; Chivers et al., 2009; Dorrepaal et al., 2009). Recently, on the basis of litter bag experiments, Dabros and Fyles (2010) studied the impact of OTCs on soil OM decomposition including nutrient supply and acidity. In contrast to the study of Dorrepaal et al. (2009) on C respired, Dabros and Fyles (2010) showed that higher air temperatures induced by 14 months of OTC treatment (i) reduced the temperature of the soil as a result of increased evapotranspiration (the paradox of "*colder soils in a*

warmer world"; Groffmann et al., 2001) and (ii) had no effect on decomposition rates of *Sphagnum* and spruce litters.

The biogeochemical processes in early peat OM decomposition still remain poorly understood and thus constitute a limiting factor in understanding the fate of C pools in peatlands (Limpens et al., 2008; Zaccone et al., 2008). Furthermore experimental *in situ* air warming have more often focused on ecosystem responses such as gas exchanges at the surface and seldom took into account organic C pools where various reactions to increased temperature may be expected (Davidson et al., 2000; Kirschbaüm, 2000; Knorr et al., 2005).

Water-extractable OM (WEOM) reflects OM decomposition (Saïd-Pullicino et al., 2007) and can therefore be a suitable indicator of consequences of experimental warming. WEOM consists of a heterogeneous mixture of more or less labile organic compounds soluble in water (Balesdent, 1996; Zsolnay, 2003) provided by both freshly decomposed litter and products of microbial metabolic activities (Charman, 2002; Zaccone et al., 2009). Within such pools, the most labile OM has mainly been studied through the analysis of sugars which are considered as readily degradable constituents used preferentially by microorganisms (Haider, 1992; Volk et al., 1997). In investigating sugar composition and its link to microbial activity, Medeiros et al. (2006) showed that some sugars such as mannitol, a polyol or reduced sugar, can also be seen as indicator of osmotic stress. On the other hand, the less labile OM of the WEOM is often investigated by way of specific ultra-violet absorbance at 280 nm ($SUVA_{280}$), which provides an estimate of aromaticity of the WEOM (Traina et al., 1990; Kalbitz et al. 2003; Weishaar et al., 2003).

The aim of the present work was to investigate the impact of *in situ* experimental air warming on WEOM properties in the upper 10 cm of peat, where most of the labile OM is decomposed. We hypothesised that peatland warming has detectable consequences on WEOM properties and that some biogeochemical parameters can be used as early indicators of changes. We considered the impact of OTCs on the peat temperature recorded at 7 cm depth. First we used the dry mass/wet mass (DM/WM) ratio and the mannitol content for assessing environmental conditions related to water table depth and/or soil humidity, and second we inferred the fate of labile and recalcitrant OM in relation to changes in decomposition processes, using water-extractable organic carbon (WEOC), isotopic composition ($\delta^{13}C$), specific UV absorbance at 280 nm ($SUVA_{280}$) and sugar composition (neutral monosaccharides, neutral disaccharides and polyols). The study was performed on the undisturbed *Sphagnum*-dominated "Le Forbonnet" peatland in a transitional poor fen site ('WET') and an open bog site ('DRY').

2. Materials and Methods

2.1. Study site

The study site is an undisturbed ombrotrophic *Sphagnum*-dominated mire situated in the Jura Mountains (The Forbonnet peatland, France, 46°49'35''N, 6°10'20''E) at an altitude of 840 m a.s.l. The site is characterized by cold winters (on average -1.4°C) and mild summers (on average 14.6°C). The annual mean temperature measured at the site over a one-year period from 5th November 2008 to 30th November 2009 was 6.5°C, and the annual precipitations 1200 mm (see also Delarue et al. in press).

Two sites were selected with respect to the functional groups of plants and hence their hydrology. The first site ('WET') was a transitional *Sphagnum*-dominated poor fen, relatively flat and homogeneous, characterized by a moss cover dominated by *Sphagnum fallax* and by the lack of *S. magellanicum*. Vascular plants such as *Eriophorum vaginatum, Vaccinum oxycoccus* and *Andromeda polifolia* were recorded in very low abundance. *Scheuchzeria palustris* and *Carex limosa* occurred outside of the studied plots. The second site ('DRY') was a *Sphagnum* bog directly adjacent to the fen area. Patterns of hummocks with *S. magellanicum, V. oxycoccos*, *E. vaginatum* and *Calluna vulgaris,* and hollows with lawns of *S. fallax, Carex rostrata* and *A. polifolia* characterized the sampling area. The terms "WET" and "DRY" are used to denote the existence of a wetness and trophic gradient inferred from the vegetation. The vegetation is known to be largely determined by water level (Wheeler and Proctor 2000; Økland et al., 2001) and the presence and dominance of *S. fallax*, *S. magellanicum and Eriophorum vaginatum* is a good indicator of environmental conditions along the gradient poor-fen with hollows and lawns, and bog with hummocks (Pedersen, 1975; Gerdol, 1995).

2.2. Experimental design, sampling and WEOM extraction

OTCs are passive warming chambers (Aronson and McNulty, 2009). They were designed following the International Tundra Experiment (ITEX) to obtain quasi-natural transmittance of visible wavelengths and to minimize the transmittance of re-radiated infrared wavelengths (Marion et al., 1997). The hexagonal chambers are made of transparent polycarbonate and are 50cm high, 1.7 m wide at the top and 2.4 m wide at the base. They were raised 10 cm above

the soil surface to allow air to circulate. Six OTCs were installed in May 2008 in the DRY and the WET sites. At each site, six plots were selected in representative surfaces and then randomly allocated to treatment. Three plots were equipped with OTCs, while three others were taken as controls. The plots were named as follows: at the DRY site, plots equipped with OTCs as DRY-OTC, and control plots as DRY-CTL; the corresponding plots at the WET site were WET-OTC and WET-CTL. Among the 12 sampling plots, the maximal distance between the two most distant plots was ca. 30 m. The monitoring of peat temperature started in November 2008 and of air temperature in July 2009. These two parameters were measured every 30 minutes at 7 cm depth and 10 cm above the soil surface respectively using thermocouple probes and datalogger (CR-1000 Campbell).

Peat cores were extracted from each plot in June 2009, after 13 months of experiment. The twelve cores (13 cm diameter, 25 cm long) were cut into 2.5 cm slices that were sub-sampled for various analyses. One subsample was dried at 50 °C for one week to measure the dry mass and the wet mass (DM/WM ratio). Another was directly frozen at -18 °C for WEOM extraction and associated analyses. It was later split into two parts. For each sub-sample, ca. 3g minced frozen peat were placed in 10 ml ultrapure water and manually homogenized for WEOM extraction. After 10 min incubation at ambient temperature (20 °C) to defrost the peat, the water extract (ultrapure water + peat water extract) was filtered through a glass fibre filter (GF6, Schleicher & Schuell, 1 μm pore size). Filtration was performed under vacuum to optimize water extraction. Ultrapure water was then added to obtain an aliquot volume of 25 ml. The first water extract was divided into two sub-aliquots: one for WEOC and δ^{13}C analyses, and one for the SUVA$_{280,}$ while the second water extract was used for carbohydrate and polyol analyses (Fig. 1).

2.3. Methods

2.3.1. Water-extractable organic carbon (WEOC) and stable carbon isotopic composition (δ^{13}C)

WEOC content and its isotopic composition were determined using liquid-chromatography-isotope ratio monitoring-mass spectrometry (LC-irMS; Thermo Isolink), in bulk mode. Prior to analysis, the samples were acidified to pH 1 (Fig. 1) with H_3PO_4 (85%). The inorganic C was eliminated by bubbling He through the mixture (ca. 5 min).

Standardisation involved a benzoic standard for WEOC analysis, and pure CO_2, IAEA and USGS simple molecule standards for $\delta^{13}C$ (Albéric et al., 2010).

2.3.2. Specific UV absorbance at 280 nm

Solutions were acidified to pH 6-7 (Fig. 1) following the recommendation of Weishaar et al. (2003). UV absorbance was measured at 280 nm using a UV spectrophotometer (Gibson®). $SUVA_{280}$ was calculated as absorbance divided by WEOC concentration (Hansson et al., 2010) and expressed as mg C^{-1} m^{-1}.

2.3.3. Neutral and reduced sugars analysis

After water extraction (Fig. 1), deoxy-6-glucose (0.4 mg ml^{-1} in water) was added as internal standard (Wicks et al., 1991). The sample was evaporated to dryness under vacuum. The sugars were then dissolved in pyridine containing 1 wt% $LiClO_4$ and left 16 h at 60°C for anomer equilibration (Bethge et al., 1996), after which they were silylated (Sylon BFT, Supelco) and analysed using a Perkin–Elmer gas chromatograph fitted with a 25 m $\times$ 0.25 mm i.d. CPSil5CB column (0.25 µm film thickness) and flame ionization detector. The oven temperature was raised from 60 to 120 °C (held 1 min) at 30 °C min^{-1}, to 240 °C at 3 °C min^{-1} and finally to 310 °C (held 10 min) at 20 °C min^{-1}. The injector split was off before injection and was turned on after 2 min. The injector was at 240 °C and the detector at 300 °C. A mixture of nine neutral monosaccharides, neutral disaccharides and polyols (fructose, glucose, mannose, sucrose, trehalose, arabitol, glycerol, inositol and mannitol) was used as external standard for compounds identification through peak retention times and for individual response coefficient determination. Concentrations are expressed in mg g^{-1} or µg g^{-1} dry mass. Replicate analyses gave an analytical precision of 5%.

2.3.4. Statistical analysis

The differences induced by OTC treatment at DRY and WET plots, in terms of air temperature, peat temperature and biogeochemical parameters were analyzed using the t-test (Statistica98 ®). Statistical significance was determined at $p < 0.05$ level. p-values comprised between 0.05 and 0.10 were considered as indicating a trend (Sullivan et al., 2008).

3. Results

3.1. OTC's warming effect on air and soil temperatures

By comparison with control plots, at both DRY and WET sites the daily mean air temperature showed a significant increase in OTCs in July, August and in September (Table 1). At the DRY site the increase reached 0.8 °C through the period considered, whereas in the WET site it ranged from 0.7 °C to 1.0°C. The maximum air temperature reached higher values in OTCs, up to 3.0°C in DRY site and up to 4.5°C in WET site (Table. 1). OTCs had no significant effect on the minimum temperature (Table 1). The rise in mean temperature can therefore be considered to be a result of the increase in maximum air temperature.

The mean peat temperature measured at 7 cm depth did not show any significant OTCs effect in DRY site (Table 1), whereas in WET site it showed a significant effect in March with an increase of 0.2 °C, which appears to be the result of a significant rise in minimum peat temperature. No significant differences in minimum peat temperature were observed in DRY site, whereas in the WET site, the minimum peat temperature was significantly higher in November, March and April under the effect of the OTCs (Table 1). The maximum peat temperature showed no significant OTC effect in neither DRY nor WET sites. Daily thermal amplitudes in the soil (Fig. 2) were higher in OTCs in April, May and June in DRY (but differences are not significant), whereas the opposite trend appears in WET (differences are significant at many periods of the year). These findings were confirmed by measurements carried out during 2010.

3.2. Water-extractable OM properties

3.2.1. Dry matter vs wet matter ratio (DM/WM)

DM/WM ratio varied from 8.9 to 6.6% in the DRY-CTL plots, and from 9.4 to 6.8% in the DRY OTC ones (Fig. 3A). Given the large standard errors, it was not possible to detect OTC effect on DM/WM ratios in the DRY situation. In the WET-CTL plots, DM/WM ranged from 8.0 to 5.9%, while it varied from 10.9 to 8.0% in the WET-OTC ones (Fig. 3B). The DM/WM ratios were higher at all depths for OTCs plots, and this difference with the control plots was significant at depths 2.5-5 cm and exhibited trends at depths 0-2.5 cm, 5-7.5 cm and 7.5-10 cm.

3.2.2. Water-extractable organic carbon (WEOC)

The WEOC content varied from 10.11 to 3.84 mg g^{-1} in DRY-CTL and from 10.28 to 3.16 mg g^{-1} in DRY-OTC (Fig. 3A), but no significant differences were observed between OTC and control plots. In contrast to the DRY site, in WET site, the WEOC content fell from 15.83 to 1.27 mg g^{-1} in WET-CTL and from 9.28 to 1.60 mg g^{-1} in WET-OTC (Fig. 3B). At soil surface (0 to 2.5 cm), the WEOC content was significantly lower in OTCs compared to control plots. With depth, WEOC decreased and the difference between OTCs and controls was still significant at 2.5-5 cm and again at 7.5-10 cm (Fig. 3B).

3.2.3. Isotopic composition ($\delta^{13}C$)

The δ^{13}C values, ranging between -27.05 and -27.88‰ for DRY-CTL and between -27.05 and -27.83‰ for DRY-OTC, with rather large standard errors, do not evidence any significant difference when compared with OTCs and controls in DRY site (Fig. 3A). At the WET site, the δ^{13}C values, ranging from -26.47 to -27.83‰ in WET-CTL and from -27.23 to -27.73‰ in WET-OTC, do not differ significantly neither (Fig. 3B), although some trends are detectable. At the surface peat (0-2.5 cm) and at depth 2.5-5 cm, the trends (with p-values of 0.08 and 0.05 respectively) indicated lower isotopic signatures in OTCs as compared to control plots, whereas the trend was reversed at depth 7.5-10 cm (p-value = 0.09).

3.2.4. Specific UV absorbance at 280 nm (SUVA$_{280}$)

The SUVA$_{280}$ index tended to increase with depth, with no significant differences between OTCs and control plots at neither DRY or WET sites (Fig. 3). Values ranged from 2.32 to 1.21 mg C l^{-1} m^{-1} in DRY-CTL and from 2.48 to 1.47 mg C l^{-1} m^{-1} in DRY-OTC. In the WET site, SUVA$_{280}$ varied from 3.46 to 0.73 mg C l^{-1} m^{-1} in WET-CTL and from 3.52 to 1.06 mg C l^{-1} m^{-1} in WET-OTC. SUVA$_{280}$ showed a trend between OTCs and control plots only at 2.5-5 cm depth (p-value = 0.07), with higher values in OTC treatment.

3.2.5. Neutral monosaccharides, disaccharides and polyols

Three types of sugars were identified in the WEOM: neutral monosaccharides, neutral disaccharides and polyols also termed reduced sugars (Table 2). The mannitol content was

221 and 344 mg g^{-1}, respectively at 2.5-5 cm and 5-7.5 cm depth in DRY-CTL, and only 88 and 81 mg g^{-1} in DRY-OTC at the same depths. Thus, in the DRY site, the OTCs induced a significant decrease in the mannitol content at these two depths. In the WET site, the mannitol content tended to increase in OTCs at 7.5-10 cm depth, (51 mg g^{-1} in WET-CTL vs. 198 mg g^{-1} in WET-OTC), whereas it tended to decrease in OTCs for fructose at 5-7.5 cm depth. In the WET site, glucose, mannose, glycerol and inositol contents exhibited also significant differences induced by OTCs but only at specific depths (Table 2). At 0-2.5 cm depth, the glycerol content was significantly lower in OTCs (169 µg g^{-1} in WET-CTL and 105 µg g^{-1} in WET-OTC). Inositol showed a significantly lower yield in OTCs at 5-7.5 cm depth (139 mg g^{-1} in WET-CTL and 12 mg g^{-1} in WET-OTC). At 7.5-10 cm depth, the glucose content was significantly higher in OTCs (0.42 mg g^{-1} in WET-CTL and 0.97 mg g^{-1} in WET-OTC). Mannose content showed the same significant pattern as glucose (3 mg g^{-1} in WET-CTL and 20 mg g^{-1} in WET-OTC). Fructose, glucose, mannose and glycerol all showed a clear decrease with depth.

4. Discussion

4.1. Impact of OTCs is different in DRY and WET sites

From July to September 2009, the mean air temperature increased by 0.7 to 1° C in the OTC plots as compared to control plots (Table 1). Subsequent measures showed that this warming also happened in 2010. Based on this significant effect (p<0.001) and considering results from many other studies on the impact of OTCs on mean air temperature (e.g., Marion et al., 1997; Hollister and Webber, 2000; Dorrepaal et al. 2004; Sullivan et al., 2008), it seems reasonable to assume that OTCs are likely to have increased the air temperature at the OTC sites also before core sampling, despite the lack of full data coverage for air temperature between the start of the experiment (May 2008) and the soil sampling date (June 2009).

In general, the effect of OTCs on the peat temperature amplitude, comparatively to controls, was more often significant during winter, with identical patterns in DRY and WET sites. In both cases, the mean amplitude was significantly lower in OTCs than in control plots, suggesting a loss of sensitivity to environmental temperature variation. As heat diffuses faster in water than in air (Rosenberg et al., 1983; Hollister, 1998), the lower temperature amplitude in peat under OTC treatment can be interpreted as the consequence of a decrease in thermal conductivity in relation to soil humidity in both DRY and WET sites, at least in winter. For

Dabros and Fyles (2010), the decrease in thermal conductivity (i) resulted from an increase in evapotranspiration and (ii) led to a decrease in average temperature. Our data do not allow us to draw such conclusions on the time scale considered. The mean and minimum temperatures in the WET sites were higher and significant under OTCs as compared to control plots only in November 2008 and March and April 2009 (Table 1). For the DRY sites, there was no evidence to support such a pattern and data tend to indicate, on the contrary, colder soils. This difference could be explained by the water level variations and/or soil humidity, and their interaction with air temperature at the boundary layer. Because of the lack of continuous measurements of humidity in air and peat, as recommended by Aerts et al. (2006) and Aronson and McNulty (2009), it was not possible to directly assign the consumption of heat by evapotranspiration. Overall, significant differences mainly appeared during winter, probably as a result of the low temperature range, which entailed a decrease in variance and thus facilitated the appearance of significant differences. During early summer time, the daily thermal amplitude (Fig. 2) indicated that in DRY sites, the temperature reached higher and lower extremes, with a tendency for OTC sites to have a higher mean temperature, whereas the contrary occurred in WET sites.

This study highlights certain difficulties using OTCs or at least for the measurement of their effect, particularly on soil temperature. It also demonstrates the need for measuring concomitantly air and soil moisture. Furthermore, in contrast to various other studies (Dorrepaal et al., 2004; Sullivan et al., 2008) in which soil temperature was determined at 5 cm depth, we did the measurements at 7 cm depth, which maybe makes it more difficult to detect induced warming. In general soil temperature is typically measured at one depth and does not take into account the phenomenon of thermal diffusion and its interactions with the "architecture" of the peat, i.e. density, which controls heat exchange and evapotranspiration (Tsuboya et al., 2001; Admiral and Lafleur, 2007). It thus appears that understanding the response of peatlands to higher air temperatures requires a thermodynamic approach combined with a better characterization of the vertical variability of physical parameters affecting thermal diffusion. Such an approach may also facilitate the understanding of the high environmental spatial variability in peatlands, as suggested by the weaker responses and the greater standard errors in DRY site as compared to WET site.

4.2. OTC-induced warming affects the dynamics of water-extractable organic matter

Since WEOM is an organic fraction extracted from wet peat using soft conditions and consists of available OM pools (Zaccone et al., 2009), it can be a suitable substrate to infer *in situ* OM dynamics, particularly under the short term effects of climate change as simulated by OTCs (13 months as for our study).

Moreover, the DM/WM ratio is likely to give straightforward information on changes in humidity and/or water table level, and is also linked to the type of bulk OM in relation to the growing vegetation. At the DRY site, this ratio did not discriminate the specific effect of OTCs (Fig. 3), but it did in the WET site resulting in higher dry matter content under OTCs. Therefore, although *in situ* continuous measurements of peat humidity were missing, we can assume that higher air temperature created by the OTC treatment at the WET sites resulted in higher evapotranspiration and thus drier soils in OTCs in comparison to control sites. Similarly, mannitol as well as the non-reducing disaccharide trehalose are considered as osmolytes that can accumulate in microbial and plant cells in response to osmotic stress such as reduction in moisture or increase in temperature (Bohnert et al., 1995; Chaturvedi et al., 1997; Waisley, 2004, Medeiros et al., 2006). Under OTCs of the DRY site, mannitol had lower concentration in the rooting zone (2.5-7.5 cm depth) and this could indicate a decrease in osmotic stress. This decrease did not correspond to a significant change in the water content of peat in the DRY site (Table 2; Fig. 3). Conversely, mannitol in the WET site, particularly at 7.5-10 cm depth, exhibited greater content under OTCs. Combined with the higher DM/WM ratio, this underlines a possible higher osmotic stress and indicates also a likely decrease of groundwater level or more probably of soil moisture under the effect of OTCs (Table 2; Fig. 3).

Unlike at the WET site, at the DRY site, except for mannitol contents, no significant changes in the WEOM parameters have been recorded between OTCs and control sites, indicating that 13 months of incubation by OTCs did not affect the WEOM dynamics. Therefore, the following discussion only focuses on the WET site.

At 0-5 cm depth at the WET site, the effect of OTCs resulted in a significant decrease of WEOC and glycerol (Table 2; Fig. 3), which could correspond to changes in the early decomposition of the peat, i.e. senescence (Thormann et al., 2007) or a change of plant composition and thus of the quality of new OM inputs. Vegetation surveys including vascular plants and mosses, using quantitative frequency measurements (Buttler, 1992) and their analysis with Redundancy analysis (RDA) showed that the site effect (DRY vs WET) was highly significant ($p < 0.001$) on vegetation communities in the two consecutive years 2008

and 2009, but that the OTC effect did not yet induce significant changes at community level ($p = 0.97$ and 0.77 for respectively 2008 and 2009). Consequently, the changes in WEOM properties cannot be assigned to a shift in vegetation composition and to consecutive changes in fresh OM inputs, but would rather be attributable to changes in senescence processes affecting OM features. Furthermore, at the same 0-5 cm depth, there was a decrease of $\delta^{13}C$ values of the WEOM as a result of ^{13}C depletion under OTCs treatement (Fig. 3). Several authors had studied factors that might influence $\delta^{13}C$ values such as vegetation species-specific pattern and photosynthetic fractionation (Smith and Epstein, 1971; Brader et al., 2010), but also the peat water content and temperature (Ménot and Burns, 2001), the nature of the microbial communities (Andrews et al., 2000) and the metabolic OM transformation (Blair et al., 1985). No OTC effect having been observed on plant communities, no impact of plant species and/or photosynthetic fractionation was to be expected. On another hand, it has previously been demonstrated in this study, that the presence of OTC entailed a lowering of the upper peat water content. Ménot and Burns (2001) admitted that carbon isotopic fractionation during photosynthesis was only weakly influenced by a moisture change from 72% to 78%. Accordingly, the change of the DM/WM ratio values here recorded might not be considered as $\delta^{13}C$ values controlling factor. Even if the peat moisture was affected by OTCs treatment, there was no evidence of a temperature change in the upper peat layers (ca. 0 to 5 cm depth). It is therefore difficult to consider temperature as a $\delta^{13}C$ values controlling factor especially as mosses and vascular plants exhibit the same photosynthetic pathways (Ménot and Burns, 2001). $\delta^{13}C$ changes might thus be mainly attributed here to microbial communities changes and consequently to OM status changes. For Zaccone et al. (2011), decay and humification processes might involve a selective degradation of OM which in turn might affect $\delta^{13}C$ value. It is also well known that (i) a relative enrichment in aromatic compounds (lignin-derived compounds and humic substances) induce a depletion of ^{13}C and more precisely that (ii) these lignin-derived compounds are generally depleted in ^{13}C by 3 to 6% relative to sugars (Benner et al., 1987; Kracht and Gleixner, 2000; Kalbitz et al., 2003). A preferential consumption of carbohydrates might thus lead to a relative enrichment in aromatic compounds with a lowering of $\delta^{13}C$ values. Specific ultra-violet absorbance ($SUVA_{280}$), which provides an estimate of the aromaticity of the WEOM (Traina et al., 1990; Weishaar et al., 2003), effectively tended to indicate a relative enrichment in aromatic compounds in the 2.5-5 cm depth interval. Although WEOC contents (strongly correlated with total sugars; $p<0.001$) tended to confirm this pattern, individual sugars did not confirm such a conclusion for the 0-5 cm peat layer (Table 2; Fig. 3). Even if our preferred hypothesis

is a stimulated WEOM decomposition in the upper peat layers under the effect of OTCs, we could not exclude an associated increase of humic substances. At 5-7.5 cm depth, sugars such as fructose and inositol showed significantly lower contents under OTCs as compared to control plots, while WEOC, $SUVA_{280}$ and $\delta^{13}C$ were not affected by OTC treatment (Fig. 3). In contrast to the soil surface, at 7.5-10 cm depth, the effect of OTCs resulted in an enrichment of $\delta^{13}C$, a slight but significant increase of WEOC, and an increase of sugar contents (Table 2; Fig. 3). Albeit the composition of the surface vegetation did not change, we cannot exclude belowground changes such as an increase of root exudates (e.g. phenolic compounds) by vascular plants, i.e. *Eriophorum vaginatum*. Such changes would be congruent with changes of $\delta^{13}C$, WEOC and sugars, and this would highlight a relative good preservation of labile dissolved OM and carbohydrates at this depth. Such preservation could be enhanced by the release of phenolic compounds, which can block enzymatic activities, allowing the most labile OM, i.e. fructose, glucose, mannose and inositol to be accumulated. It has been shown that phenolics produced by *Sphagnum* have a potential inhibitor effect on fungal and bacterial breakdown activity and/or on enzymes implied in OM decomposition (Wetzel, 1992; Fenner et al., 2005; Opelt et al., 2007; Mellegard et al., 2009).

5. Conclusion

This study highlights some difficulties in predicting peatland OM response to a rise in air temperature:

- It appears that peat temperature alone is not sufficient for characterizing the impact of OTCs on environmental conditions. There is a need for continuous measurements of humidity at the soil surface and in peat for understanding thermal diffusion at air-soil interface and towards depth;

- The differences in warming responses between DRY and WET sites indicate that spatial variability is a key component in understanding the fate of peatland C in a perspective of global warming;

- Our results, which cover a 1 yr simulated warming and thus only reflect a single season, must be extrapolated with caution. Even if the plant assemblage did not show significant changes during such a short duration, below ground changes such as a shift in root biomass and/or exudates cannot be excluded.

Despite the short duration of the OTC manipulative warming, WEOM shows, at the WET site, (i) a relative enrichment of aliphatic and/or aromatic compounds due to the increased

consumption of WEOC in the upper peat layers and (ii) an accumulation of WEOC and sugars in the deeper layers, probably as an effect of increased phenolic compounds leached by roots. Beyond these patterns our work shows that WEOM, in some moisture conditions, is an efficient indicator for understanding early decay processes and the fate of OM.

Acknowledgments

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Table 1 Effects of OTCs on temperatures of air (10 cm above soil surface) and peat (at -7 cm depth) during a 3-months period (July to September 2009) for air temperature and during a 8-months period (November 2008 to June 2009) for soil temperatures in DRY and WET sites[a].

Table 2 Effect of OTCs on neutral monosaccharides (fructose, glucose and mannose), neutral disaccharides (sucrose and trehalose) and polyol contents (mg g^{-1} or µg g^{-1}) in the surface peat (0-10 cm) of the OTC plots and control (CTL) plots in DRY and WET sites Significant differences between OTCs and controls are indicated by p-values in bold (n = 3).

Fig. 1. Sampling strategy and flowchart for sample treatment and analysis

Fig. 2. Daily thermal amplitudes (°C) of peat (at -7 cm depth) in the control plots (empty symbols) and the OTC plots (black symbols) in both DRY (A) and WET (B) sites. Significant differences between OTCs and controls are indicated (* $p < 0.05$; ** $p < 0.01$; n = 3).

Fig. 3. Effect of OTCs on dry matter – wet matter (DM/WM) ratio, water-extractable organic carbon (WEOC content - mg g^{-1}), isotopic C signature (δ^{13}C - ‰) and specific ultra-violet absorbance at 280 nm (SUVA$_{280}$ - l mg C^{-1} m^{-1}) in surface peat (0-10 cm) of the OTC (black symbols) and control (empty symbols) plots from DRY (A) and WET (B) sites. Mean values and standard errors are given. Significant differences between OTCs and controls are indicated (* $p < 0.05$; ** $p < 0.01$; n = 3).