

EXPRESS LETTER

Isotope composition of bulk carbon in replicated *Sphagnum* peat cores from three Central European high-elevation wetlands

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Several processes may contribute to systematic downcore trends in $\delta^{13}\text{C}$ of bulk *Sphagnum* peat. Whereas changes in water availability during C assimilation may change $\delta^{13}\text{C}$ values in both a negative and positive direction, other processes would always cause a uni-directional shift in $\delta^{13}\text{C}$. Selective preservation of isotopically light lignin C may lead to more negative $\delta^{13}\text{C}$ values with an increasing depth and age of peat. Anthropogenic change toward lower $\delta^{13}\text{C}$ of atmospheric CO_2 due to massive coal burning since the beginning of the Industrial Revolution would result in lower $\delta^{13}\text{C}$ of the youngest peat layers, and in higher $\delta^{13}\text{C}$ of older peat layers. Emissions of low- $\delta^{13}\text{C}$ methane from wetlands should result in a progressive enrichment of the residual peat substrate in the heavier isotope ^{13}C . Consequently, deeper peat would have higher $\delta^{13}\text{C}$. In a specific peat profile, the downcore trend in $\delta^{13}\text{C}$ will be the result of an interplay between all these isotope-sensitive processes. Most Central European wetlands studied previously show a ^{13}C enrichment (i.e., higher $\delta^{13}\text{C}$ values) with an increasing depth and age. Here we focus on sites which showed lower $\delta^{13}\text{C}$ with an increasing depth and age when a single peat core was taken. Replication did not confirm this negative downcore $\delta^{13}\text{C}$ shift. A positive downcore $\delta^{13}\text{C}$ shift is more widespread than previously believed. We suggest that decreasing $\delta^{13}\text{C}$ of atmospheric CO_2 and emissions of low- $\delta^{13}\text{C}$ methane belong to the main controls of the downcore $\delta^{13}\text{C}$ trends in young peat substrate.

Keywords: peat, *Sphagnum*, carbon, C sequestration, isotopes

INTRODUCTION

Peatland ecosystems are characterized by a substantial accumulation of organic matter, resulting from a long-term excess of net primary production at the surface over decomposition throughout the peat column. Peatlands cover over 4 million km^2 of the Earth's land surface, and store 455 Pg of carbon, nearly one third of the world's soil C pool (Gorham, 1995). At present, the mid-latitude, boreal and subarctic peatlands are thought to be a net sink for atmospheric CO_2 and simultaneously a major net source of atmospheric CH_4 (Wieder and Vitt, 2006), both being important greenhouse gases. Exchanges of gases between the atmosphere and peatlands are governed by the balance between C assimilation and mineralization, both of which are temperature-dependent (Dise *et al.*, 1993). There is a general agreement that climatic warming will be most pronounced in northern latitudes (IPCC, 2007). Therefore, the relationship between C cycling in peatlands and climate has emerged as a major question.

In the course of climatic warming, higher emanations of greenhouse gases, accompanying thinning of peat deposits, may lead to further temperature increases, and thus accelerate climatic warming (Woodwell and Mackenzie 1995; Novak *et al.*, 2008a).

Peat decomposition, and in particular C mineralization to CO_2 and CH_4 , depends not only on temperature, but also on organic matter quality. Many researchers have measured fluxes of CO_2 and CH_4 from wetlands under field conditions and from peat monoliths upon laboratory manipulation of water table level and temperature (Whalen and Reeburgh, 2000; von Fisher and Hedin, 2002; Yavitt *et al.*, 2005). Carbon stable isotopes are a useful tool to constrain global budgets of greenhouse gases and to identify missing sources and sinks of these gases (Bouwman, 1999). Carbon isotope ratios of CO_2 and CH_4 have often been measured in peat bogs and incubated peat cores (Chanton *et al.*, 1992; White *et al.*, 2008). Typically, $\delta^{13}\text{C}$ of biogenic methane can be as low as -60‰ , more than 30‰ lower than that of peat substrate (see Wieder and Vitt, 2006 for a critical review). Surprisingly few studies have focused on bulk C isotope composition of the solid peat substrate (Novak *et al.*, 1999; Jedrysek and Skrzypek, 2005). Data on $\delta^{13}\text{C}$ of solid peat are needed to complement isotope signatures of the ema-

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nating gases in isotope mass balance considerations. Before $\delta^{13}\text{C}$ trends in ageing peat can be linked with isotope signatures of greenhouse gases, the role of other processes affecting $\delta^{13}\text{C}$ must be evaluated. Processes that can obscure a possible isotope record of methane emanations from the peat substrate are: 1) change in water availability during assimilation; 2) change in $\delta^{13}\text{C}$ of atmospheric CO_2 during the Industrial Revolution; and 3) selective preservation of organic macro-molecules during peat diagenesis. The first step in evaluating the role of various isotope-sensitive processes during peat accretion is to determine whether vertical $\delta^{13}\text{C}$ trends in peat are site-specific, or whether some more general trends emerge from between-site comparisons.

In this study we selected three mountain-top *Sphagnum*-dominated peat bogs, and tested whether they exhibit a similar downcore $\delta^{13}\text{C}$ shift when multiple cores per site are analysed.

METHODOLOGICAL APPROACH

Between 1992 and 2006, we collected vertical peat cores from 10 mainly ombrotrophic (rain-fed) peat bogs throughout the Czech Republic, Central Europe. The C-isotope analysis focussed on the topmost ~40 cm of the accreting peat, which, based on ^{210}Pb dating, represents the last 150–200 years (Vile *et al.*, 2000). The overall downcore $\delta^{13}\text{C}$ trends were positive in most, but not all,

peat cores when one peat core per site was available (Novak *et al.*, 2008b). For the present study, we selected two sites (BS and MM), which in the previous study did *not* show a positive downcore $\delta^{13}\text{C}$ shift, revisited them in 2007, and collected three separate peat cores per site. The mean $\delta^{13}\text{C}$ values are reported here, along with mean $\delta^{13}\text{C}$ values for a third randomly selected site (TA).

All three sites (Fig. 1, Table 1) are situated at elevations higher than 700 meters and are extremely wet most of the year, with water table within several centimeters of the capitula of growing *Sphagnum*. No microtopographical differences (hummocks and hollows) were observed in the sampled segments of unforested bog lawns. The dominant *Sphagnum* species were *S. fallax Klinggr.* at TA and MM, and *S. tenellum* at BS. The distance between each of the three replicated cores was more than 80 meters at each site.

ANALYTICAL PROCEDURE

Peat cores, 10-cm in diameter, collected in the summer of 2007, were sectioned into 2 cm thick segments, dried, weighed, homogenized and analyzed for C concentrations (Elemental Analyzer Fisons 1108) and $\delta^{13}\text{C}$ values (Finnigan MAT 251 mass spectrometer). All data are reported in per mil vs. the V-PDB standard, with the reproducibility of the C isotope analysis better than $\pm 0.3\text{‰}$.

RESULTS

Vertical trends in mean $\delta^{13}\text{C}$ values of bulk peat for the three study sites, along with standard errors ($n = 3$), are given in Fig. 2a. Across the sites, the mean $\delta^{13}\text{C}$ values ranged between -28.0 and -24.2‰ . At the peat surface, BS had the highest, and MM the lowest $\delta^{13}\text{C}$ value. Carbon in the deepest sampled peat layer (*ca.* 40 cm below surface) was isotopically heavier (i.e., had higher $\delta^{13}\text{C}$) than the topmost sample at all three sites. A general slight increase in $\delta^{13}\text{C}$ values with an increasing peat depth was seen at TA and BS. At MM, there were two intervals of increasing $\delta^{13}\text{C}$ downcore (1 to 17 cm, and 33 to 45 cm), with an offset to more negative values in the middle of the profile (Fig. 2a).



Fig. 1. Study sites.

Table 1. Study site characteristics

Site	Location	Elevation (m.a.s.l.)	Mean annual temperature (°C)	Mean annual precipitation (mm)
BS	50°50' N, 15°18' E	980	4.0	1231
MM	50°14' N, 17°19' E	780	6.2	1155
TA	50°00' N, 12°42' E	940	5.0	934

DISCUSSION

Before evaluating the importance of site-specific vs. general trends in $\delta^{13}\text{C}$ in vertical peat profiles, we made an attempt to remove noise from the C isotope data. Table 2 illustrates one approach of how to remove noise from vertical $\delta^{13}\text{C}$ trends in peat. Using ^{210}Pb dates by Vile *et al.* (2000) and C concentrations (Fig. 2b), we calculated mass-weighted $\delta^{13}\text{C}$ of all peat layers younger than 100 years, and mass-weighted $\delta^{13}\text{C}$ of all sampled peat layers older than 100 years. This approach has the advantage of ascribing more weight to the isotope signature of deeper peat, which has higher density and represents a longer time span per each 2-cm than younger and shallower peat. As seen in Table 2, older peat had higher mass-weighted $\delta^{13}\text{C}$ than younger peat at one site, BS (1.1‰). The increase in $\delta^{13}\text{C}$ in older peat at the two remaining sites, MM and TA (0.1 and 0.3‰, respectively), was small, relative to the analytical uncertainty (<0.3‰). None of the sites showed lower $\delta^{13}\text{C}$ values in peat older than 100 years compared to peat younger than 100 years.

Before discussing individual isotope-selective processes, possibly affecting $\delta^{13}\text{C}$ in bulk peat cores, the changing $\delta^{13}\text{C}$ of the atmospheric CO_2 must be considered. It provides the carbon source for plant uptake and

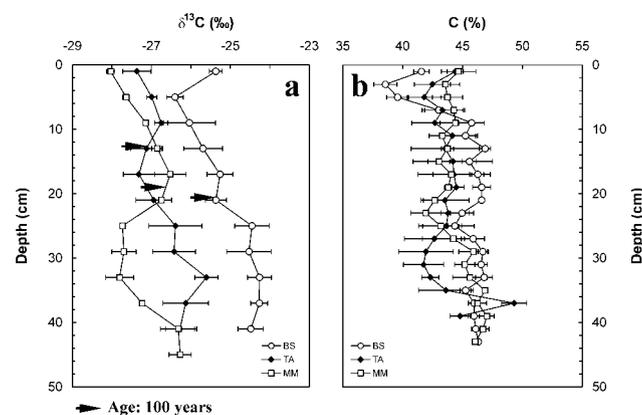


Fig. 2. Isotope composition (a), and concentration (b) of total carbon in three peat bogs. Number of peat cores per site $n = 3$, error bars denote standard error.

thus represents the primary input into the studied system. The sizeable increase in atmospheric CO_2 concentrations over the past 200 years due to fossil fuel burning has been accompanied by lowering of its $\delta^{13}\text{C}$ (2‰ since the early 1800s; Friedli *et al.*, 1986). Our observations (Fig. 2a, Table 2) are not contradictory to this mechanism of lowering $\delta^{13}\text{C}$ upcore. It remains to be seen whether the predominance of a positive downcore $\delta^{13}\text{C}$ shift in Central Europe (four sites in Novak *et al.*, 2008b, and BS in this study) is also typical of wetlands under other climatic conditions.

While fossil-fuel burning may contribute to changing $\delta^{13}\text{C}$ in young peat cores, we note that both in aerated forest soils and wetland soils, the common positive downcore $\delta^{13}\text{C}$ shift is almost always accompanied by a positive downcore shift in $\delta^{15}\text{N}$ (Nadelhoffer and Fry, 1988; more than 20 sites in the US) and $\delta^{34}\text{S}$ (Novak *et al.*, 1994; nine sites in the US and Europe). There is no evidence to suggest that atmospheric species of reactive nitrogen and reactive sulfur have been changing toward lower $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ values due to fossil fuel burning, or any other recent anthropogenic activity. Therefore, some studies suggested that the simultaneous increase in $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ in organic soils may have an analogical explanation, diagenesis (Nadelhoffer and Fry, 1988; Novak *et al.*, 1999; Novak *et al.*, 2003; sites different from the current study). Before we discuss C selectivity of peat diagenesis, three more potential sources of C isotope variability in young peat should be mentioned.

We do not know whether *Sphagnum* species composition at our study sites was constant or changed over the past 150 years. Changes in species compositions, however, were shown previously to have no effect on $\delta^{13}\text{C}$ of *Sphagnum* (Rice, 2000).

The site-specific $\delta^{13}\text{C}$ value of living *Sphagnum* is controlled by the magnitude of the assimilation-related isotope fractionation, which, in turn, depends on the availability of water. Lower water content leads to lower external diffusion resistance and larger C isotope fractionation, resulting in lower $\delta^{13}\text{C}$ of *Sphagnum* (Price *et al.*, 1997). If microclimatic conditions do not change over time, the difference between $\delta^{13}\text{C}$ of peat at any depth and $\delta^{13}\text{C}$ of local *Sphagnum* could be viewed, at least

Table 2. Comparison of $\delta^{13}\text{C}$ in shallower and deeper peat taking into consideration peat density and carbon concentration

Site	Mass-weighted $\delta^{13}\text{C}$ of peat younger than 100 years*	Mass-weighted $\delta^{13}\text{C}$ of peat older than 100 years, down to the deepest sampled layer
BS	-25.8	-24.7
MM	-27.1	-27.0
TA	-26.9	-26.6

* ^{210}Pb dates adopted from Vile *et al.* (2000).

partly, as a result of peat diagenesis. More realistically, microclimatic conditions at TA, BS and MM did change over time. This makes it more difficult to evaluate the magnitude of a diagenesis-related $\delta^{13}\text{C}$ fractionation in peat.

While changes in water availability may change $\delta^{13}\text{C}$ of *Sphagnum* in both a negative and positive direction, degradation of organic molecules in deeper peat is a unidirectional process. Some previous studies indicated that selective preservation of lignin relative to cellulose may result in systematic trends in $\delta^{13}\text{C}$ over time. Since $\delta^{13}\text{C}$ of lignin is lower than that of the fast decomposing cellulose (Benner *et al.*, 1987), the expected isotope effect is lower $\delta^{13}\text{C}$ downcore. As seen in Fig. 2a, this explanation is not consistent with our data. Our unpublished data on $\delta^{13}\text{C}$ of lignin in *Sphagnum* peat indicate that with an increasing age of lignin, its $\delta^{13}\text{C}$ increases, while the relative abundance of lignin in older peat also increases.

Peat diagenesis will likely result in a positive $\delta^{13}\text{C}$ shift in the residual substrate, if a significant amount of isotopically light C is being preferentially removed in the form CH_4 , whose $\delta^{13}\text{C}$ may be more than 30‰ lower than that of the bulk peat substrate (Wieder and Vitt, 2006). We propose that this is a feasible mechanism for a widespread general shift toward higher $\delta^{13}\text{C}$ with an increasing peat depth and age. In the case of terminal carbon mineralization to CO_2 in peat, no major isotope difference is seen between organic C and CO_2 . We note that in aerated forest soils, which emit mineralized carbon as CO_2 and not CH_4 , Nadelhoffer and Fry (1988) also ascribed the positive $\delta^{13}\text{C}$ shift toward deeper soil horizons to diagenesis. These authors carefully evaluated a number of alternative explanations for higher $\delta^{13}\text{C}$ in deeper soil, and concluded that there may be a minute isotope effect in aerobic terminal C mineralization to CO_2 . Nadelhoffer and Fry (1988) simultaneously did not rule out an effect of changing $\delta^{13}\text{C}$ of atmospheric CO_2 on soil $\delta^{13}\text{C}$ systematics.

CONCLUSIONS

None of the study sites exhibited a clear-cut negative downcore trend in $\delta^{13}\text{C}$ of peat substrate when three peat cores were collected per site. At each site, the deepest analyzed peat layer, taken from a depth of approximately 40 cm below surface, had higher $\delta^{13}\text{C}$ than living *Sphagnum*. Across the sites, peat older than 100 years had a $\delta^{13}\text{C}$ value on average 0.5‰ higher than peat younger than 100 years. At one site, BS, $\delta^{13}\text{C}$ in older peat was larger (1.1‰) than the analytical uncertainty (0.3‰). The observed downcore $\delta^{13}\text{C}$ gradients in *Sphagnum* peat bogs are consistent with progressive enrichment of the residual substrate in the heavier isotope ^{13}C during early peat diagenesis, with a possible contribution of a decreasing

$\delta^{13}\text{C}$ of atmospheric CO_2 during the most recent 200 years caused by massive fossil fuel burning.

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