

# The effect of a reciprocal peat transplant between two contrasting Central European sites on C cycling and C isotope ratios

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**Abstract.** An 18-month reciprocal peat transplant experiment was conducted between two peatlands in the Czech Republic. Both sites were 100% *Sphagnum*-covered, with no vascular plants, and no hummocks and hollows. Atmospheric depositions of sulfur were up to 10 times higher at the northern site Velke jerabi jezero (VJJ), compared to the southern site Cervene blato (CB). Forty-cm deep peat cores, 10-cm in diameter, were used as transplants and controls in five replicates. Our objective was to evaluate whether CO<sub>2</sub> and CH<sub>4</sub> emissions from *Sphagnum* peat bogs are governed mainly by organic matter quality in the substrate, or by environmental conditions. Emission rates and  $\delta^{13}\text{C}$  values of CO<sub>2</sub> and CH<sub>4</sub> were measured in the laboratory at time  $t = 18$  months. All measured parameters converged to those of the host site, indicating that, at least in the short-term perspective, environmental conditions were a more important control of greenhouse gas emissions than organic carbon quality in the substrate. Since sulfate reducers outcompete methanogens, we hypothesized that the S-polluted site VJJ should have lower methane emissions than CB. In fact, the opposite was true, with significantly ( $p < 0.01$ ) higher methane emissions from VJJ. Additionally, as a first step in an effort to link C isotope composition of emitted gases and residual peat substrate, we determined whether multiple vertical  $\delta^{13}\text{C}$  profiles in peat agree. A high degree of within-site homogeneity in  $\delta^{13}\text{C}$  was found. When a specific vertical  $\delta^{13}\text{C}$  trend was seen in one peat core, the same trend was also seen in all the remaining peat cores from the wetland.

The  $\delta^{13}\text{C}$  value increased downcore at both CB and VJJ. At VJJ, however, 20 cm below surface, a reversal to lower  $\delta^{13}\text{C}$  downcore was seen. Based on <sup>210</sup>Pb dating, peat at 20-cm depth at VJJ was only 15 years old. Increasing  $\delta^{13}\text{C}$  values in VJJ peat accumulated between 1880–1990 could not be caused by assimilation of atmospheric CO<sub>2</sub> gradually enriched in the light isotope <sup>12</sup>C due to fossil fuel burning. Rather they were a result of a combination of isotope fractionations accompanying assimilation and mineralization of *Sphagnum* C. These isotope fractionations may record information about past changes in C storage in wetlands.

## 1 Introduction

It is estimated that one third of global soil carbon is stored in wetlands, mainly at northern latitudes (Woodwell, and Mackenzie, 1995). According to most atmospheric circulation models, it is these northern latitudes where global warming will be most pronounced during the 21st century (IPCC, 2007). Microbial activities and solubilities of dissolved gases are strongly temperature-dependent (Moore et al., 1998). Therefore, recent studies have focused on whether thinning of peat deposits and higher emissions of greenhouse gases may contribute to stronger climate forcing, and *accelerate* temperature increases (Updegraff et al., 2001; Yavitt et al., 2005). Using inverse modelling, Mikaloff Fletcher et al. (2004) showed greater importance of the wetland global source of CH<sub>4</sub> than previously thought. Some carbon (C) sequestration studies have suggested that local hydrological factors are more important than climate (Yu et al., 2001). For Holocene peat profiles, concave plots of total mass



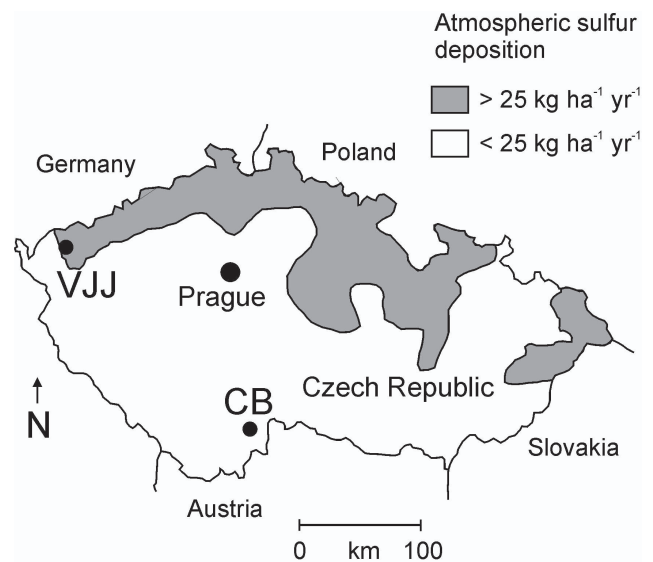
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vs. age have indicated continuous decomposition throughout the peat column (Wieder and Vitt, 2006). Over time, the efficiency of peatlands as atmospheric C sinks diminishes (Beleyea, and Clymo, 2001).

Part of C photosynthesized in peatlands is returned to the atmosphere as CO<sub>2</sub>. Autotrophic and heterotrophic respiration comprise ca. one third of CO<sub>2</sub> uptake via photosynthesis (Heikkinen et al., 2002). Methane is formed either from acetate dissimilation (acetate pathway) or bicarbonate reduction (hydrogen pathway). In northern peatlands, acetate pathway dominates in shallow anaerobic peat layers, benefiting from warm summers and a relatively large supply of fresh labile organic matter from the acrotelm. The importance of the hydrogen pathway increases at greater peat depths with lower availability of labile organic carbon molecules (Hornibrook et al., 1997).

Isotopes can be used to constrain the global budgets of greenhouse gases, including CO<sub>2</sub> and methane (Bouwman, 1999). When isotope abundances in an atmospheric gas change, a shift in sources or sinks of the gas is indicated. Thus, isotopes may be instrumental in identifying a previously unknown source or sink of greenhouse gases. Anaerobic decay produces CH<sub>4</sub> depleted in <sup>13</sup>C, and CO<sub>2</sub> enriched in <sup>13</sup>C, relative to the source substrate (Gu and Schelske, 2004). Several attempts have been made to isotopically link two complementary reservoirs of carbon, solid peat substrate, and atmospheric gases (Lansdown et al., 1992; Jedrysek et al., 2005; Clymo and Bryant, 2008; Knorr et al., 2008). The δ<sup>13</sup>C values can potentially be a useful tracer of past methane emissions because biogenic methane contains isotopically extremely light C (Woodwell, and Mackenzie, 1995). Can removal of this isotopically light C from peat be detected in isotopically heavier residual organic C remaining in situ? An analysis of various aspects of this question was presented by Clymo and Bryant (2008). Before any isotope mass balance considerations are made, the degree of within-site and between-site homogeneity in δ<sup>13</sup>C values of vertical peat profiles must be assessed. Upscaling the results of research plot studies is possible only if a variety of sites exhibit similar isotope features. Our first objective was to isotopically analyze bulk C in a number of replicate peat cores within two contrasting *Sphagnum* wetlands, and compare the vertical δ<sup>13</sup>C profiles. We discuss possible explanations of the found vertical δ<sup>13</sup>C profiles in solid peat.

Our second objective was related to the fact that the current rate of increase in methane concentrations in the atmosphere is lower than several decades ago (Dise and Verry, 2001). Suggestions have been made that elevated sulfur depositions in industrial countries have led to suppression of methane emissions from wetlands and rice paddies (Wieder and Vitt, 2006). Thermodynamically, anaerobic bacterial sulfate reduction outcompetes methanogenesis (Lamers et al., 2002; Blodau, and Moore, 2003). We used a sharp north-south pollution gradient in Central Europe to investigate whether higher S inputs lead to lower rates of methanogenesis.



**Fig. 1.** Location of the studied peatlands. Sulfur pollution contours from Novak et al. (2005).

Our third objective was to evaluate whether CO<sub>2</sub> and CH<sub>4</sub> emission rates in *Sphagnum* peat bogs are governed mainly by organic matter quality in the substrate, or by environmental conditions. Again, we used the north-south pollution gradient in Central Europe, and conducted a reciprocal peat transplant experiment between a highly polluted and a relatively unpolluted *Sphagnum* bog. Reciprocal transplants of organic soil among contrasting sites were previously used to study the effect of site-specific controls on biogeochemical (Mulligan and Gignac, 2001; Keller and Bridgman, 2007; Westbrook et al., 2006) and biological (Sohlenius and Bostrom, 1999) variables. Reciprocal *Sphagnum* transplant experiments were performed by Wieder and Yavitt (1994), Yavitt and Wieder (2000), and Yavitt et al. (2005). We hypothesized that if organic matter quality in the substrate, i.e., the ratio between labile and recalcitrant C forms, is the primary control of terminal C mineralization, the emissions of CO<sub>2</sub> and CH<sub>4</sub> from the host site will remain similar to those at the home site. If environmental parameters are the primary control, the emissions of CO<sub>2</sub> and CH<sub>4</sub> will become similar to the host site.

## 2 Materials and methods

### 2.1 Study sites

The two peat bogs selected for the reciprocal transplant experiment (Fig. 1, Table 1) represented extremes in atmospheric S deposition. The northern site, Velke jerabi jezero (VJJ), is located in the “Black Triangle” region, one of the most polluted parts of the world. The Black Triangle comprises the northern Czech Republic, southeast Germany

**Table 1.** Characteristics of the studied peat bogs.

Site	Location	Elevation (m)	Mean annual temperature (°C)	Annual precipitation (mm)	Annual sulfur deposition <sup>a</sup> (kg ha <sup>-1</sup> )	Annual nitrogen deposition <sup>a</sup> (kg ha <sup>-1</sup> )	Bog water pH
Velke jerabi jezero (VJJ)	50°24' N 12°36' E	930	4.0	1000	28.7	23.4	3.0–5.5
Cervene blato (CB)	48°52' N 13°47' E	450	7.8	600	7.6	11.8	2.5–5.0

<sup>a</sup> Atmospheric S and N inputs into semi-open peat bogs were calculated as arithmetic mean of open-area deposition and spruce canopy throughfall.

**Table 2.** *Sphagnum* species present at the two study sites.

VJJ	CB
<i>S. fallax</i> v. <i>Klinggr.</i>	<i>S. fallax</i> v. <i>Klinggr.</i>
<i>S. riparium</i> Angstr.	<i>S. magellanicum</i>
<i>S. girgensonii</i> Russ.	<i>S. capillifolium</i>
<i>S. russowii</i> Warnst.	<i>S. augustifolium</i>
<i>S. acutifolium</i>	<i>S. cuspidatum</i>

and southern Poland. VJJ is situated in the Krusne hory Mts. near a cluster of coal-fired power plants, which were built in the 1950s, but had desulphurization units installed only in the mid-1990s. Spruce (*Picea abies*) stands died back on 1000 km<sup>2</sup> in the Black Triangle between 1975 and 1995, partly as a result of high atmospheric SO<sub>2</sub> concentrations. In the vicinity of VJJ (25 km north-west of the power plants), symptoms of crown thinning and needle yellowing were observed. The industrial air pollution in the area peaked in 1987, with the highest spruce throughfall of 160 kg S ha<sup>-1</sup> yr<sup>-1</sup> recorded at the nearby Jezeri (Novak et al., 2005). After 1987, industrial emission rates decreased rapidly, and are now 90% lower.

The southern site, Cervene blato (CB, Fig. 1, Table 1), is located in the relatively unpolluted Trebon Basin, a natural preserve near the Czech border with Austria. The bog is surrounded by healthy mature spruce stands. The distance between CB and VJJ is 220 km. CB is currently four times less polluted with atmospheric S and twice less polluted with reactive forms of atmospheric N, compared to VJJ.

## 2.2 Design of peat transplant experiment

A total of 30 peat cores, 40-cm long, 10-cm in diameter, were collected in April 2002 using polyvinylchloride (PVC) cylinders with a sharpened bottom edge. Fifteen peat cores were collected at VJJ and 15 peat cores at CB. All cores were taken from peat lawns whose surface was 100% *Sphagnum*-covered, with no vascular plants. Predominating *Sphagnum* species are given in Table 2. Five cores from each site were

transported to the laboratory and analyzed. At each site, additional five cores were transplanted back to their original positions. Before replacing the five cores into the soil at their home sites, the cores were removed from the PVC cylinders, wrapped individually with plastic mesh (openings 2.5 mm × 2.5 mm), leaving the surface free. The mesh was fastened around each peat core and secured with cable ties. At each site, the remaining five cores were capped and placed vertically into a cooler for immediate transport to the host site. Five replicate peat cores were transplanted from VJJ to CB, and five replicate cores from CB to VJJ. Upon arrival at the host site, the five peat cores were removed from PVC cylinders, wrapped with mesh and inserted into the positions of five local peat cores, which had been previously collected and transported to their host site.

The transplanted cores remained in the soil for 18 months. In September 2003, we retrieved 10 cores from VJJ (five control cores originating from VJJ and five transplanted cores originating from CB) and 10 cores from CB (five control cores originating from CB and five transplanted cores originating from VJJ). The cores were transported to the laboratory.

Cylindrical incisions in peat may impact the field experiments (see Yavitt et al., 2005 and references therein). For example, exudate dynamics of severed roots are affected for several hours. The length of our experiment (18 months), however, permits equilibrium to be reached soon after its beginning. In a transplanted peat core, pore water of the host site replaces pore water of the home site within several days after insertion into its new position. The reason is high hydraulic conductivity in topmost 30 to 40 cm of the bog.

In month 18, we were able to recover peat cores that were somewhat shorter than peat cores analyzed at time 0 (30 vs. 40 cm). With no roots of vascular plants, peat at the bottom of the cores was nearly fluid and some of it may have been lost by advection of bog water when being transplanted.

One 50-cm long, 10-cm in-diameter, peat core was collected from each VJ and CB in April 2002 for <sup>210</sup>Pb dating of peat accretion history.

### 2.3 Analysis

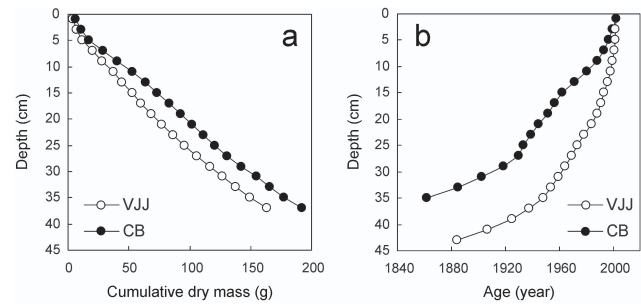
Five 40-cm long peat cores per site taken into the laboratory at time  $t = 0$  (April 2002) were frozen, cut into 2-cm thick segments, dried at 60 °C, weighed, and homogenized. Ash content was determined on a 0.5 g aliquot at 550 °C. Carbon concentrations were measured on a Carlo Erba Elemental Analyzer and corrected for ash content, C isotope compositions were determined on a Finnigan MAT 251 mass spectrometer following on-line combustion of the peat. Carbon isotope data are given in the usual notation as  $\delta^{13}\text{C}$  values relative to the V-PDB standard. Reproducibility of  $\delta^{13}\text{C}$  determinations was better than  $\pm 0.3\%$ .

The two 50-cm long peat cores were processed as above. Three grams of pulverized peat from each 2-cm section were digested with HCl and HNO<sub>3</sub>, spiked with <sup>209</sup>Po as a chemical yield tracer, and <sup>210</sup>Po, along with <sup>209</sup>Po were plated on Ag discs (Vile et al., 2000). Polonium activities were measured on an EG&G Ortec 576 A dual  $\alpha$  spectrometer, and <sup>210</sup>Pb dates calculated.

A 27-hour laboratory incubation study was performed to assess CO<sub>2</sub> and methane emission potentials from transplanted and control peat cores extruded in September 2003. The duration of the incubation was chosen in accord with previous studies that reported linearity of both CO<sub>2</sub> and methane emission rates over time (Vile et al, 2003; Turetsky, and Ripley, 2005). Three peat cores were randomly selected from each of the following four treatments: CB cores extruded from CB, CB cores extruded from VJJ, VJJ cores extruded from VJJ, and VJJ cores extruded from CB. The headspace was purged with N<sub>2</sub> for 10 min. The 12 capped peat cores were anaerobically incubated at 20 °C and gas samples taken 2, 4, 8, 12 and 27 h after the beginning of the incubation. At each time, 60 mL of headspace gas were removed using a syringe and injected into an evacuated Hungate tube. An additional 60 mL of N<sub>2</sub> were added to each headspace for vacuum prevention, and headspace dilution corrections were made. Concentrations of CO<sub>2</sub> and CH<sub>4</sub> were determined on a Shimadzu 14A gas chromatograph. Rates of CO<sub>2</sub> and CH<sub>4</sub> emissions were estimated from changes in headspace concentrations over time. Hungate tube content was transferred by He carrier into a line for trace gas measurements. CO<sub>2</sub> was collected in a condensation trap, CH<sub>4</sub> was combusted over Pd catalyst. The  $\delta^{13}\text{C}$  values were determined with reproducibility better than  $\pm 0.5\%$ .

Following the 27-hour laboratory incubation, the 10 peat cores previously transplanted to their host site (five from CB to VJJ, and five from VJJ to CB) were frozen, cut into 2-cm thick segments, dried at 60 °C, weighed, and homogenized. Bulk C concentrations and  $\delta^{13}\text{C}$  values were determined for each 2-cm thick peat segment.

Statistical analysis was performed using linear mixed models (Laird and Ware, 1982) and the R 2.6.2 software (R Development Core Team, 2008). For CO<sub>2</sub> and CH<sub>4</sub> emissions, a linear mean evolution was used with random in-



**Fig. 2.** Peat accretion history. (a) cumulative dry mass, (b) <sup>210</sup>Pb dates.

tercept and slope for each sample to account for only conditional independence of repeated observations. Using the method of restricted maximum likelihood, estimates of the mean intercepts, mean slopes, covariance matrix and residual variance were computed. The estimated mean evolution of CO<sub>2</sub> and CH<sub>4</sub> emissions is shown in Figs. A1 and A2 in the Electronic Annex (<http://www.biogeosciences.net/7/921/2010/bg-7-921-2010-supplement.pdf>).

## 3 Results

### 3.1 Peat accretion history

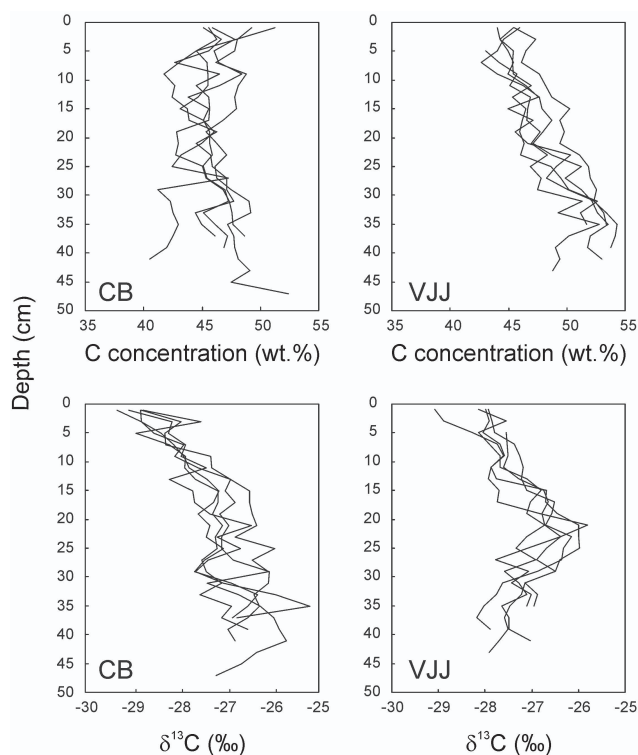
Cumulative dry mass increased smoothly with an increasing depth and age at both sites, and was slightly higher at CB than at VJJ (Fig. 2a). Lead-210 dates revealed faster peat accumulation at the northern, colder site VJJ, compared to the southern, warmer site CB (Fig. 2b). At a depth of 34 cm, peat at CB was 140 years old, whereas peat at VJJ was just 55 years old.

### 3.2 Downcore C concentration trends

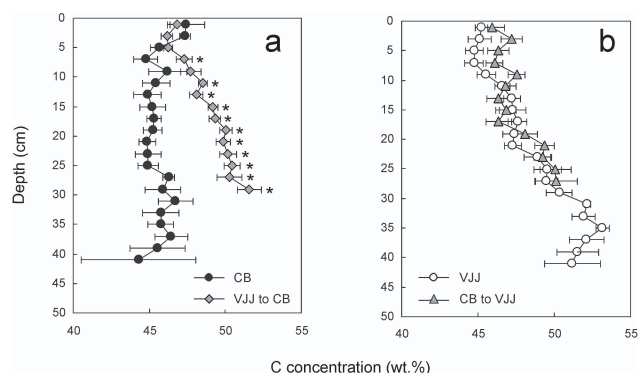
The vertical C concentration patterns differed between the two sites (Fig. 3). Whereas C concentrations at VJJ steadily increased with an increasing peat depth, those at CB showed no vertical gradient.

### 3.3 Downcore $\delta^{13}\text{C}$ trends

Also the vertical trends in  $\delta^{13}\text{C}$  values of bulk peat differed between the two sites (Fig. 3). With an increasing depth, peat at CB became progressively enriched in the heavier isotope <sup>13</sup>C (higher  $\delta^{13}\text{C}$  values). In contrast, peat from VJJ exhibited a clear-cut  $\delta^{13}\text{C}$  maximum at a depth of 20 cm below surface. Between 0 and 20 cm, peat at VJJ became progressively enriched in the heavier isotope <sup>13</sup>C, similar to CB. However, at depths greater than 20 cm, peat at VJJ became progressively enriched in the lighter isotope <sup>12</sup>C, and the  $\delta^{13}\text{C}$  values decreased with increasing depth. Importantly, at both sites, when a specific vertical  $\delta^{13}\text{C}$  trend was seen in one peat core,



**Fig. 3.** Carbon concentration and  $\delta^{13}\text{C}$  values in replicated peat cores.

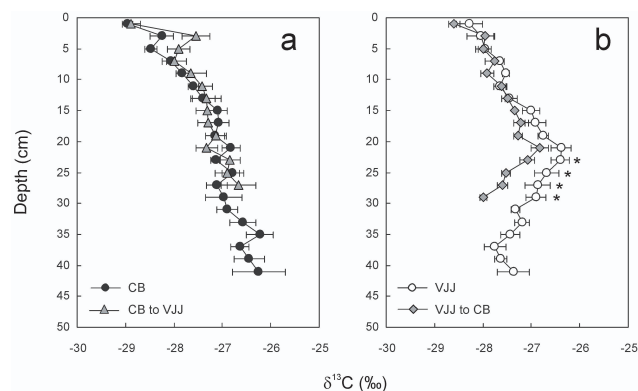


**Fig. 4.** Effect of the peat transplant on C concentration (means  $\pm$  SE,  $n = 5$ ). Asterisks denote statistically significant differences ( $p < 0.05$ ).

the same trend was also seen in all the remaining peat cores. There was a high degree of within-site homogeneity in vertical  $\delta^{13}\text{C}$  trends.

### 3.4 The effect of peat transplant on substrate C

Figures 4 and 5 show mean C concentrations and  $\delta^{13}\text{C}$  values for five replicate peat cores per treatment, along with standard errors. The four treatments are marked as follows: “CB” are peat cores taken from CB to the laboratory at the begin-



**Fig. 5.** Effect of the peat transplant on  $\delta^{13}\text{C}$  values (means  $\pm$  SE,  $n = 5$ ).

ning of the experiment. “VJJ” are peat cores taken from VJJ to the laboratory at the beginning of the experiment. “CB to VJJ” are peat cores originating from CB which were transplanted to VJJ for 18 months, and then analyzed. “VJJ to CB” are peat cores originating from VJJ, which were transplanted to CB for 18 months, and then analyzed.

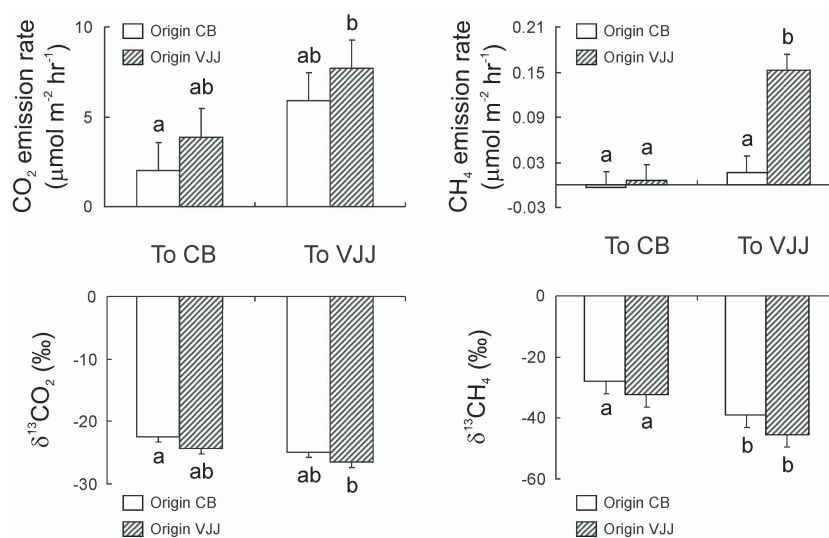
As seen in Fig. 4, transplanting peat cores from VJJ to CB had no effect on the vertical C concentration gradient: both sets of peat cores originating from VJJ had higher C concentrations at greater depth than at peat surface (cf., Fig. 4a and 4b). CB peat cores had similar C concentrations at all depths. When peat cores were transplanted from CB to VJJ, higher C concentrations were seen at greater depths. The CB to VJJ carbon concentration profiles were similar to VJJ concentrations at the beginning of the experiment (Fig. 4b). A complementary representation of the C concentration data is in Fig. A5 (Electronic Annex (<http://www.biogeosciences.net/7/921/2010/bg-7-921-2010-supplement.pdf>)); an overlay plot for CB and CB to VJJ).

As seen in Fig. 5, transplanting peat cores between sites had little effect on their vertical  $\delta^{13}\text{C}$  trends. CB to VJJ peat cores exhibited higher  $\delta^{13}\text{C}$  values downcore, identical to CB peat cores (Fig. 5a). VJJ to CB peat cores exhibited a peak in  $\delta^{13}\text{C}$  values at 20-cm depth, similar to VJJ peat cores (Fig. 5b).

### 3.5 Emissions of $\text{CO}_2$ and $\text{CH}_4$ from incubated peat

The 27-hour incubation was performed on peat cores taken into the laboratory at time  $t = 18$  months. The four preceding treatments (transplant types) included: CB to CB, CB to VJJ, VJJ to VJJ and VJJ to CB. Detailed time series of concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  and their  $\delta^{13}\text{C}$  values during the 27-hour incubation are depicted in Figs. A1–A4 in the Electronic Annex (<http://www.biogeosciences.net/7/921/2010/bg-7-921-2010-supplement.pdf>).  $\text{CO}_2$  concentrations increased linearly in all four treatments. Methane concentrations increased in three treatments during the first 12 h.





**Fig. 6.** The concentration and C isotope composition of CO<sub>2</sub> and methane emanating from peat at the end of the transplant experiment (mean ± SE,  $n = 3$ ). Different letters denote statistically significant differences ( $p < 0.05$ ).

### 3.6 Comparison of CO<sub>2</sub> and CH<sub>4</sub> emissions among treatments

Figure 6 compares CO<sub>2</sub> and CH<sub>4</sub> emission rates and  $\delta^{13}\text{C}$  values among the four transplant types, obtained from the 27-hour laboratory incubation. All data in Fig. 6 were measured at room temperature (20°C). For both CO<sub>2</sub> and CH<sub>4</sub>, the same relative magnitude of emission rates was observed: CB to CB had the lowest gas emission rates, VJJ to VJJ had the highest gas emission rates. CO<sub>2</sub> emissions from the peat cores kept at their home site VJJ were almost four times higher than CO<sub>2</sub> emissions from the peat cores kept at their home site CB. Methane emissions from the peat cores kept at their home site VJJ were nine times higher than those in any other treatment. Interestingly, all four measured parameters in every graph in Fig. 6 (concentrations and isotope compositions of CO<sub>2</sub> and CH<sub>4</sub>) had converged to parameters of their host site by the end of the transplant experiment. Transplanting peat cores from CB to VJJ resulted in a 3.5-fold increase in CO<sub>2</sub> emission, approaching that of the host site. Transplanting peat cores from VJJ to CB resulted in a 50% decrease in CO<sub>2</sub> emissions, approaching those of the host site. A similar pattern was seen for methane emissions, e.g., transplanting peat cores from VJJ to CB resulted in 15 times lower methane emissions compared to the home site VJJ.

### 3.7 Comparison of $\delta^{13}\text{C}$ -CO<sub>2</sub> and $\delta^{13}\text{C}$ -CH<sub>4</sub>

Also the  $\delta^{13}\text{C}$  values of both gases emitted from transplanted peat cores converged to those of the host site (Fig. 6). The  $\delta^{13}\text{C}$  values of both CO<sub>2</sub> and methane were lower for VJJ to VJJ peat cores than for CB to CB peat cores. The peat cores producing more CO<sub>2</sub> and methane at their home location (i.e., VJJ) always had isotopically lighter carbon. In

general, transplanting peat cores to a host site resulted in either a decrease or an increase in  $\delta^{13}\text{C}$  so that the C isotope composition became more similar to the host site (Fig. 6).

## 4 Discussion

### 4.1 C sequestration in peat

Over millennia, peat deposits developing in colder climate tend to accumulate more carbon and are thicker compared to peat deposits developing in warmer climate (Yu et al., 2001; Beleya, and Baird, 2006). Such a relationship was found for VJJ and CB for the most recent 150 years. The mean annual temperature at the northern site VJJ is 3.8 °C lower compared to the southern site CB. The vertical growth rate of VJJ was twice that of CB (Fig. 2b). Substrate accumulates whenever the rates of net primary production are greater than the rates of decomposition. While higher temperature leads to higher *Sphagnum* growth, also the decomposition rate is greater. Lower net primary production at lower temperature is usually associated with slower decomposition. A number of records of recent peat show similar litter additions and decay rates despite climatic differences (Belyea and Clymo, 2001; Wieder and Vitt, 2006; Novak et al., 2008). The positive relationship between C accumulation and colder climate valid for entire Holocene deposits is not always valid for the top-most peat layers. Net primary production appears to be more sensitive to environmental parameters than decay (Moore et al., 1998). The main difference between VJJ and CB is in fertilization levels by anthropogenic nutrients (Table 3). Higher availability of nutrients at VJJ may have played a role in peat accumulation (see Sect. 4.8). Temperature may not be the main control of the greater peat accumulation at VJJ.

**Table 3.** Concentration of nutrients in surface peat bog waters. Years of sampling: 2002–2003, number of samples  $n = 12$  per site. Means  $\pm$  standard errors ( $\text{mg L}^{-1}$ ) are given.

	VJJ	CB
$\text{Ca}^{2+}$	$2.71 \pm 0.36$	$2.75 \pm 0.30$
$\text{Mg}^{2+}$	$0.58 \pm 0.09$	$1.01 \pm 0.13$
$\text{Na}^+$	$2.47 \pm 0.23$	$0.92 \pm 0.09$
$\text{K}^+$	$1.96 \pm 0.61$	$1.61 \pm 0.31$
$\text{NH}_4^+$	$0.42 \pm 0.17$	$0.20 \pm 0.06$
$\text{NO}_3^-$	$0.33 \pm 0.06$	$0.24 \pm 0.03$
$\text{SO}_4^{2-}$	$9.82 \pm 1.31$	$0.92 \pm 0.12$

Two more aspects of peat accumulation at VJJ and CB bear mention. First, the peat accumulation rates at our sites are unusually high compared to other sites in the temperate climate zone. This is illustrated in Fig. A6, in which depth vs. age profiles of VJJ and CB are compared to 10 different sites in Europe and the US. More peat (and thus C) accumulation at the Czech sites is seen especially in layers older than 50 years.

Second, previous studies have documented that *Sphagnum* growth rates differ between species (Vitt et al., 2003; Asada, and Warner, 2005), and that following extended periods of exposure to nutrients, *Sphagnum* species distribution may change (Hobbie et al., 2000). Also the decay rate is affected by species, e.g., *S. fuscum* decays more slowly than *S. cuspidatum* (Johnson, and Dammon, 1991). At our sites, a number of various *Sphagnum* species are present (Table 2), and so far we have no indication of a relationship between the *Sphagnum* species community and peat accumulation rate.

Several authors have questioned the validity of  $^{210}\text{Pb}$  dating of peat accretion history (Urban et al., 1990). However, Pb immobility in peat was verified experimentally (Vile et al., 1999). Turetsky et al. (2004) published a critical review of the potential of residual  $^{210}\text{Pb}$  activities as a dating tool, and of techniques used to corroborate  $^{210}\text{Pb}$  dates in peat.

#### 4.2 Controls on $\delta^{13}\text{C}$ of ageing peat

The  $\delta^{13}\text{C}$  values of vertical peat profiles are a useful tool for studying maturation and diagenesis of peat if four conditions are met: (i)  $\delta^{13}\text{C}$  gradients exist in peat substrate with age, (ii)  $\delta^{13}\text{C}$  gradients are widespread, (iii) C maturation in peat is isotopically selective, and (iv) other isotope-selective processes can be distinguished from peat maturation. As seen from Figs. 3 and 5, clear-cut vertical  $\delta^{13}\text{C}$  signals are found in *Sphagnum* peat. From peat surface to a depth of 15–20 cm, these signals (higher  $\delta^{13}\text{C}$  downcore) seem to be common (Knorr et al., 2008). In contrast, we do not know of any other peatland where a systematic decrease in  $\delta^{13}\text{C}$  downcore (such as the one starting at a depth of 20 cm at VJJ) was reported.

A small kinetic C isotope fractionation during peat degradation was reported by Wynn et al. (2006). In an open system, Rayleigh distillation may result in isotopically heavier residual C in situ while low- $\delta^{13}\text{C}$  is removed. Indeed, biogenic methane can have  $\delta^{13}\text{C}$  values as low as  $-110\%$ . There is an analogy between degradation of organic C in well-aerated upland soils, and wetland soils. For upland soils, Nadelhoffer and Fry (1988) concluded that mineralization-related preferential release of the light isotope  $^{12}\text{C}$  may contribute to higher  $\delta^{13}\text{C}$  in deeper soil horizons. Isotopically heavier residuum in deeper soils has been reported also for N (Nadelhoffer, and Fry, 1988 and references therein, Novak et al., 2003), and for S (Novak et al., 1996, 2005). Degradation of organic S-containing molecules in peat also preferentially releases the light isotope  $^{32}\text{S}$  (Novak et al., 1994, 1999).

Two processes linked to assimilation of atmospheric  $\text{CO}_2$  by plants can mask a possible C isotope effect of peat degradation. Burning of fossil fuels over the past 200 years has injected into the atmosphere isotopically light  $\text{CO}_2\text{-C}$  (Friedli et al., 1986), and this lower  $\delta^{13}\text{C}$  (decrease of 2‰ since the early 1800s) may be seen in the uppermost layers of organic upland soils. While this effect is well documented, we propose that it is not the dominant control of  $\delta^{13}\text{C}$  values in young peat layers in our study. As seen in Figs. 3 and 5, gradual admixture of isotopically light fossil-fuel C from the atmosphere is not consistent with the VJJ  $\delta^{13}\text{C}$  profile below the depth of 20 cm. When moving upward, higher, instead of lower,  $\delta^{13}\text{C}$  were observed. In these peat layers, dating from the early and mid-20th century (Fig. 2), admixture of the industrial low- $\delta^{13}\text{C}$  carbon is not seen. Instead, the lower  $\delta^{13}\text{C}$  at greater depth at VJJ could be explained by drier conditions before 1987 (the year corresponding to the 20-cm peat depth). Lower water content leads to lower external  $\text{CO}_2$  diffusion resistance, and greater C-isotope discrimination upon assimilation. If so,  $\delta^{13}\text{C}$  records in peat could be used as a geochemical archive of site-specific moisture conditions.

Under different climatic conditions, different *Sphagnum* species predominate. If the climate changes at a single site, this may result in a third process that may mask a diagenesis-related downcore shift in  $\delta^{13}\text{C}$  of peat substrate. An assumption would be that different *Sphagnum* species carry different  $\delta^{13}\text{C}$  signatures. Rice (2000), however, showed that changes of species composition had no effect on  $\delta^{13}\text{C}$  of *Sphagnum*. Skrzypek et al. (2007) found that higher temperature leads to slightly lower  $\delta^{13}\text{C}$  of *Sphagnum* cellulose within the same species. Loader et al. (2007) found small differences in  $\delta^{13}\text{C}$  of stems, pendants and horizontal branches of *S. capillifolium*.

#### 4.3 The C isotope mass balance approach

Clymo, and Bryant (2008) studied a 7-meter deep peat deposit in the UK. Their results illustrate that closing a historical C isotope budget may be difficult, due to several poorly understood parameters. At the UK site,  $\delta^{13}\text{C}$  values

of bulk peat substrate and DOC did not change with depth and were close to  $-27\text{‰}$ . In contrast, porewater methane C was isotopically much lighter ( $-70\text{‰}$ ). The  $\delta^{13}\text{C}$  value of porewater  $\text{CO}_2$  increased with increasing peat depth from ca.  $-10$  to  $+10\text{‰}$ . DOC and dissolved gases at each depth were hundreds to thousands years younger than solid peat. The amount of  $\text{CO}_2$  in pore water was 5–10 times greater than the amount of  $\text{CH}_4$ . In case of methane production via acetate fermentation, we would expect the same magnitude of two opposite C isotope shifts relative to  $\delta^{13}\text{C}$  of the source substrate (more negative  $\delta^{13}\text{C}$ - $\text{CH}_4$ , and more positive  $\delta^{13}\text{C}$ - $\text{CO}_2$ ), but also the same concentrations/fluxes of both gases. Neither was observed (Clymo and Bryant, 2008). The unknown parameters include  $\delta^{13}\text{C}$  of historical emissions of  $\text{CO}_2$  and  $\text{CH}_4$ , and differences in diffusion coefficients of  $^{12}\text{C}$  and  $^{13}\text{C}$  of dissolved gases. Hornibrook et al. (2000) reported a confounding factor for C isotope systematics in peat profiles: at greater depths, autotrophically formed acetate may be present, leading to somewhat lower fractionation than otherwise would be expected in the  $\text{CO}_2$ -reduction dominated part of deep catotelm (typical fractionation factors  $\alpha < 1.032$  for acetoclastic methanogenesis and 1.045–1.082 for hydrogenotrophic methanogenesis; Whiticar, 1999). Hornibrook et al. (1997) found increasing  $\delta^{13}\text{C}$ - $\text{CO}_2$  and decreasing  $\delta^{13}\text{C}$ - $\text{CH}_4$  values from peat surface to a depth of 1 m (from  $-12$  to  $-6\text{‰}$ , and from  $-55$  to  $-65\text{‰}$ , respectively), attributing them mainly to a switch from the acetate to the hydrogen pathway of methanogenesis. Steinmann et al. (2009) found, similar to Clymo and Bryant (2008), also 5 times higher dissolved  $\text{CO}_2$  concentrations compared to  $\text{CH}_4$  in deep peat, and interpreted the difference as a result of more intense ebullition of methane, which is the less soluble of the two gases.

Knorr et al. (2008) manipulated water table level in peat monoliths in a 300-day experiment, and applied the isotope mass balance approach to individual depth segments. The  $\delta^{13}\text{C}$  value of solid substrate was  $-27.1$  to  $-27.7\text{‰}$ . The  $\delta^{13}\text{C}$  value of emitted  $\text{CO}_2$  was between  $-20$  and  $-23\text{‰}$ , i.e., higher than  $\delta^{13}\text{C}$  of the substrate (heavier C). Our data do not permit construction of an isotope mass balance similar to that of Knorr et al. (2008), due to a different sampling protocol. However, we note that a major problem associated with these calculations is uncertainty related to the soil mass. A very small error in dry mass (or presence of silicate grains) affects the uncertainty of the gas partitioning, for example, of the flux of an anaerobically produced  $\text{CO}_2$ . The reason is much lower mass of the gas compared to the mass of the soil. We encountered this difficulty in our previous work, specifically when calculating  $\delta^{34}\text{S}$  of emanating  $\text{H}_2\text{S}$  in laboratory soil incubations (Novak et al., 2001).

#### 4.4 Decoupling of C concentrations and $\delta^{13}\text{C}$ in peat profiles

In intact peat profiles, increasing C concentrations at greater depth are often viewed as a manifestation of substrate degradation, with faster removal of functional -OH groups than removal of carbon (Wieder and Yavitt, 1994). Surprisingly, we found that, in some sample types, the two signs of substrate degradation were decoupled. For example, at CB,  $\delta^{13}\text{C}$  values increased downcore, possibly reflecting substrate degradation (emission of low- $\delta^{13}\text{C}$  methane), while C concentration did not increase. Further study is needed to ascertain how common the decoupling of C concentration and isotope trends in maturing peat is.

#### 4.5 Linking sulfate reduction and methane emission

Atmospheric S inputs at VJJ were four times higher than at CB at the time of the transplant experiment, and 10 times higher 15 years earlier (Novak et al., 2005). Table 3 illustrates that sulfate concentration in pore water at VJJ is still 10 times higher compared to CB, despite easing atmospheric pollution. Because microbial sulfate reducers out-compete methanogens (Dise, and Verry, 2001), we expected higher methane emissions at CB than at VJJ. In fact, the opposite was true, and peat cores originating from the polluted site VJJ had nine times higher  $\text{CH}_4$  emission rate than other peat cores. Methane emissions at CB were close to zero. This is an unexpected result, because the most obvious explanation, the presence of vascular plants, is ruled out. There were no vascular plants on the research plots. Vascular plants contain conduits transporting methane directly to the atmosphere, protecting it from oxidation in the acrotelm. The measured emission rates of methane at our sites were affected by methane oxidation, which mainly takes place at the lower edge of the green *Sphagnum* plants. This is documented by  $\delta^{13}\text{C}$ - $\text{CH}_4$  values in the range of  $-20$  to  $-45\text{‰}$ , a result of preferential oxidation of low- $\delta^{13}\text{C}$  methane (Chanton, 2005). Fresh biogenic methane has  $\delta^{13}\text{C}$  values between  $-50$  and  $-110\text{‰}$ , depending on the methanogenic pathway (Wieder and Vitt, 2006).

#### 4.6 Comparison of $\delta^{13}\text{C}$ - $\text{CO}_2$ and $\delta^{13}\text{C}$ - $\text{CH}_4$ in incubated peat and in the field

The ranges of  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  and methane in our incubation experiment were quite narrow (Fig. 6), and different from those reported by previous studies. Landsdown et al. (1992), for example, reported  $\delta^{13}\text{C}$ - $\text{CH}_4$  values of  $-73\text{‰}$  (isotopically lighter C compared to CB and VJJ) and  $\delta^{13}\text{C}$ - $\text{CO}_2$  values of around  $-2\text{‰}$  (isotopically heavier C compared to CB and VJJ). In Table 4 we summarized unpublished C isotope data for  $\text{CO}_2$  and methane, captured in a passive chamber at CB and VJJ under field conditions. The field data exhibited greater variability in  $\delta^{13}\text{C}$ - $\text{CH}_4$  values ( $-7.5$



**Table 4.** Concentrations and  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  and methane emitted from VJJ and CB *Sphagnum*-covered bog surfaces. The gas samples were taken on 9 July 2002 (VJJ), and 11 July 2002 (CB) under ambient air temperature of  $20 \pm 2^\circ\text{C}$ . SE=standard error.

	VJJ		CB	
	$\text{CO}_2$ [ppm]	$\delta^{13}\text{C}\text{-CO}_2$ (‰)	$\text{CO}_2$ [ppm]	$\delta^{13}\text{C}\text{-CO}_2$ (‰)
	821	-14.1	829	-15.6
	4930	-13.8	30 500	-16.7
	648	-12.1	959	-20.6
mean $\pm$ SE	$2130 \pm 1400$	$-13 \pm 1$	$11\,000 \pm 9870$	$-18 \pm 2$
	$\text{CH}_4$ [ppm]	$\delta^{13}\text{C}\text{-CH}_4$ (‰)	$\text{CH}_4$ [ppm]	$\delta^{13}\text{C}\text{-CH}_4$ (‰)
	66	-7.5	61	-17.9
	20	-23.2	141	-22.6
	368	-40.8	16	-18.4
mean $\pm$ SE	$151 \pm 109$	$-24 \pm 10$	$73 \pm 37$	$-20 \pm 1$

to  $-40.8\text{‰}$ ), compared to the laboratory incubation ( $-31.3$  to  $-52.7\text{‰}$ ). On average, carbon of both  $\text{CO}_2$  and  $\text{CH}_4$  was isotopically heavier in the field than in the laboratory incubation. This was true for both sites. The laboratory conditions (identical for all treatments) resulted in a somewhat lower degree of methane oxidation than under field conditions.

We offer a similar explanation also for the observed lower  $\delta^{13}\text{C}$  values of both  $\text{CO}_2$  and methane at VJJ compared to CB in the laboratory (Fig. 6). VJJ exhibited higher  $\text{CO}_2$  and methane emission rates than CB. In peat cores from both sites with the same water level during incubation, methane oxidation was more similar than methane production. Thus a lower percentage of the produced methane was oxidized at VJJ, leaving behind isotopically lighter methane C compared to CB (freshly produced  $\text{CH}_4$  has a very low  $\delta^{13}\text{C}$  value on average close to  $-70\text{‰}$ ). In local peat cores from both sites, C of  $\text{CO}_2$  was isotopically somewhat heavier than C of methane, providing additional evidence of methane oxidation (Fig. 6).

#### 4.7 The effect of peat transplant on $\text{CO}_2$ and $\text{CH}_4$ emissions

The main objective of the reciprocal peat transplant experiment was to evaluate whether organic carbon quality in the substrate, or environmental parameters are the main control of  $\text{CO}_2$  and  $\text{CH}_4$  emission rates. At the studied depths, peat from VJJ was younger and the substrate could potentially provide more labile organic C than the substrate from CB. If organic C quality in the substrate was the main control of greenhouse gas emissions, we would expect high  $\text{CH}_4$  emissions from VJJ peat transplanted to CB. That was not observed. Over the 18 months of the experiment, metabolism and trace gas emissions from all transplanted peat cores converged to those of the host sites (Fig. 6). This allows us to conclude that environmental parameters were by far the dominant control of terminal C mineralization potentials at our study sites. Availability of labile C forms in solid peat played

a much less significant role, as illustrated by a dramatic suppression of  $\text{CH}_4$  emissions when VJJ peat was transplanted to CB (Fig. 6). The role of DOC will be discussed separately in Sect. 4.9.

#### 4.8 Effect of elevated inputs of nutrients on C cycling in shallow peat

Aerts et al. (2003) found in a 12-year field manipulation study, during which N and P were added to a riparian peatland and grassland, that the initial plant community was the main determinant of C losses through decomposition. Nutrient additions enhanced litter production, but had no effect on litter decomposition (i.e., on terminal C mineralization, and, by implication, also on greenhouse gas emissions). In contrast, Limpens and Berendse (2003) concluded from a litterbag study that *Sphagnum* decomposition was stimulated by nitrogen deposition. Bragazza et al. (2006) showed along a European pollution transect that increased N availability resulted in higher  $\text{CO}_2$  emissions and increased DOC production. Increased N availability favoured microbial decomposition by removing N constraints on microbial metabolism, by higher litter quality, and by stimulated microbial enzymatic activity. As seen in Table 3, VJJ bog waters had higher concentrations of both  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , compared to CB. Based on the existing literature, we suggest that the higher industrial pollution of the northern site VJJ may have contributed to higher  $\text{CO}_2$  emission rates. In theory, also methane production may be enhanced by a slight nutrient enrichment through higher production of free aminoacids and sugars.

#### 4.9 The role of DOC

Microbial populations in peat core transplanted to a host site start using the local DOC for their metabolism within hours to days, due to high permeability of the substrate to the lateral flow of local pore waters. In this respect, DOC resembles

environmental parameters of the host site, (temperature, atmospheric deposition of nutrients/pollutants) which also start affecting the imported substrate almost immediately.

In general, DOC production decreases with increasing peat depth. The contribution of recent *Sphagnum* photosynthate C to DOC may be as much as 4% (Fenner et al., 2004). As mentioned previously, Clymo and Bryant (2008) found younger  $^{14}\text{C}$  ages in individual depth levels of a peat bog compared to in-situ peat substrate. This agrees with the finding of Chasar et al. (2000) that recently photosynthesized DOC is transported downcore. Fresh DOC laterally entering transplanted peat cores plus freshly formed plant exudates may affect C cycling by supplying labile organic C forms (Crow and Wieder, 2005). At our sites, we did not study individual chemical C forms in DOC, however, DOC concentrations were known. During the growing season, with the water table only 2 cm below *Sphagnum* capitula, Hruska (1994) reported significantly higher DOC concentrations at CB (95–101 mg L<sup>-1</sup>), compared to any other peat bogs in the Czech Republic. Other sites in the south near CB had 7 to 35 mg DOCL<sup>-1</sup>. VJJ and other sites in the north of the country had 5 to 42 mg DOCL<sup>-1</sup>. We conclude that DOC concentrations themselves do not explain higher rates of terminal C mineralization at VJJ compared to CB.

## 5 Conclusions

Sensitivity of carbon cycling in peatlands to various environmental parameters, such as mean annual temperature and sulfur and nitrogen deposition, was studied at two *Sphagnum*-dominated peat bogs in Central Europe. Both sites were waterlogged throughout the year, with negligible differences in hydrology. It was found that the colder northern site VJJ accumulated more organic carbon over the past 150 years than the southern warmer site CB. The emission rates of both products of terminal C mineralization, CO<sub>2</sub> and CH<sub>4</sub>, were also higher at the colder site VJJ. One possible explanation is that peat at the northern site VJJ had been continuously fertilized since the beginning of the Industrial Revolution. While net primary productivity increased due to higher nutritional status of the northern site, decomposition rates, which are believed to be less sensitive to environmental parameters, were also higher at the northern than at the southern site. The difference between organic mass production and decomposition was still higher at the northern site compared to the southern site.

Since microbial sulfate reducers outcompete methanogens, we hypothesized that the sulfur-polluted site VJJ should have lower methane emissions than CB. However, the opposite was true, with higher methane emissions from VJJ. This finding cannot be explained by presence of vascular plants at VJJ, known to facilitate methane transport to the atmosphere, because such plants were not found at the sampling sites.

A replicated peat transplant experiment revealed that imported peat adjusted its carbon cycling to that of the host site. It follows that the organic carbon quality of the substrate did not control C transformation rates. Rather, environmental parameters, such as nutritional status, were the main controls of C storage in the wetland. Fluxes of CO<sub>2</sub> and CH<sub>4</sub> from the peat to the atmosphere were controlled mainly by local plus imported microbial communities, metabolizing DOC of local porewaters under local environmental and nutritional conditions.

Extensive replication of peat monoliths, needed for a peat transplant experiment, was used for a complementary C isotope study of both the solid substrate and emitted gases, CO<sub>2</sub> and CH<sub>4</sub>. Vertical  $\delta^{13}\text{C}$  trends in solid peat exhibited a high degree of within-site homogeneity, but were site specific. In all 20 studied peat cores, the  $\delta^{13}\text{C}$  value increased downcore in the topmost ca. 20 cm. This trend could have been caused by both preferential removal of the light isotope  $^{12}\text{C}$  from older peat due to decomposition, or by growing fossil fuel burning which spikes  $^{12}\text{C}$ -rich CO<sub>2</sub> into the atmosphere. In peat deeper than 20 cm at VJJ, however,  $\delta^{13}\text{C}$  increased upcore. VJJ peat at the 20 cm depth was relatively young (year 1987). Between 1880 and 1987, fossil fuel burning was already adding isotopically light CO<sub>2</sub>-C to the atmosphere, and could not have dominated the increasing  $\delta^{13}\text{C}$  trend upcore at VJJ. Consequently, a different C isotope selective mechanism must have dominated the C isotope systematics between 1880 and 1987 at VJJ, overprinting both peat degradation and fossil-fuel derived C input. This mechanism might be related to historical moisture conditions (most severe 150 years ago), because droughts lead to greater C-isotope discrimination during photosynthesis. In general, both assimilation of atmospheric C by *Sphagnum*, and decay of *Sphagnum*, are associated with C isotope fractionation, which may potentially serve as an archive of past changes in the peatland C sink. Dry conditions lead to lower  $\delta^{13}\text{C}$  values of *Sphagnum*, substrate maturation (itself depending on climate) leads to higher  $\delta^{13}\text{C}$  values of the residual organic matter. The vertical  $\delta^{13}\text{C}$  profile in peat is a result of an interplay of these isotope selective processes. The steepness of the downcore  $\delta^{13}\text{C}$  shift may contain information about cumulative removal of isotopically light C via methane production.

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## References

- Aerts, R., De Caluwe, H., and Beltman, B.: Plant community mediated vs. nutritional controls on litter decomposition rates in grasslands, *Ecology*, 84, 3198–3208, 2003.
- Asada, T. and Warner, B. G.: Surface peat mass and carbon balance in a hypermaritime peatland, *Soil Sci. Soc. Amer. J.*, 69, 549–562, 2005.
- Belyea, L. R. and Baird, A. J.: Beyond “The limits to peat bog growth”: Cross-scale feedback in peatland development, *Ecol. Monographs*, 76, 299–322, 2006.
- Belyea, L. R. and Clymo, R. S.: Feedback control of the rate of peat formation, *Proc. Biol. Sci.*, 268, 1315–1321, 2001.
- Blodau, C. and Moore, T. R.: Micro-scale CO<sub>2</sub> and CH<sub>4</sub> dynamics in a peat soil during a water fluctuation and sulfate pulse, *Soil Biol. Biochem.*, 35, 535–547, 2003.
- Bouwman, A. F.: Developments in Atmospheric Science 24, Approaches to scaling of trace gas fluxes in ecosystems, Elsevier Science, 372 pp., 1999.
- Bragazza, L., Freeman, C., Jones, T., Rydin, H., Limpens, J., Fenner, N., Ellis, T., Gerdol, R., Hajek, M., Hajek, T., Lacumin, P., Kutnar, L., Tahvanainen, T. and Toberman, H.: Atmospheric nitrogen promotes carbon loss from peat bogs, *Proc. Natl. Acad. Sci. USA*, 103, 19386–19389, 2006.
- Chanton, J. P.: The effect of gas transport on the isotope signature of methane in wetlands, *Organic Geochem.*, 36, 753–768, 2005.
- Chaser, L. S., Chanton, J. P., Glaser, P. H., Siegel, D. I., and Rivers, J. S.: Radiocarbon and stable carbon isotopic evidence for transport and transformation of dissolved organic carbon, dissolved inorganic carbon, and CH<sub>4</sub> in a northern Minnesota peatland, *Global Biogeochem. Cy.*, 14, 1095–1108, 2000.
- Clymo, R. S. and Bryant, C. L.: Diffusion and mass flow of dissolved carbon dioxide, methane, and dissolved organic carbon in a 7-m deep raised peat bog, *Geochim. Cosmochim. Ac.*, 72, 2048–2066, 2008.
- Crow, S. E. and Wieder, R. K.: Sources of CO<sub>2</sub> emission from a northern peatland: Root respiration, exudation and decomposition, *Ecology*, 86, 1825–1834, 2005.
- Dise, N. and Verry, E.: Suppression of peatland methane emission by cumulative sulfate deposition in simulated acid rain, *Biogeochemistry*, 53, 143–160, 2001.
- Fenner, N., Ostle, N., Freeman, C., Sleep, D. and Reynolds, B.: Peatland carbon efflux partitioning reveals that *Sphagnum* photosynthate contributes to the DOC pool, *Plant Soil*, 259, 345–354, 2004.
- Friedli, H., Lotscher, H., Oeschger, H., Siegenthaler, U. and Stauffer B.: Ice core record of the <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric CO<sub>2</sub> in the past two centuries, *Nature*, 324, 237–238, 1986.
- Gu, B., Schelske, C. L., and Hodell, D. A.: Extreme <sup>13</sup>C enrichments in a shallow hypereutrophic lake: Implications for carbon cycling, *Limnol. Oceanogr.*, 49, 1152–1159, 2004.
- Heikkinen, J. E. P., Elsakov, V. and Martikainen, P. J.: Carbon dioxide and methane dynamics and annual carbon balance in tundra wetland in NE Europe, Russia, *Global Biogeochem. Cy.*, 16, 1115, doi:10.1029/2002GB001930, 2002.
- Hobbie, S. E., Schimel, J. P., Trumbore, S. E. and Randerson, J. R.: Controls over carbon storage and turnover in high-latitude soils, *Global Change Biol.*, 6, 196–210, 2000.
- Hornibrook, E. R., Longstaffe, F. J. and Fyfe W. S.: Spatial distribution of microbial methane production pathways in temperate zone wetland soils: Stable carbon and hydrogen isotope evidence, *Geochim. Cosmochim. Ac.*, 61, 745–753, 1997.
- Hornibrook, E. R., Longstaffe, F. J., and Fyfe W. S.: Evolution of stable carbon isotope compositions for methane and carbon dioxide in freshwater wetlands and other anaerobic environments, *Geochim. Cosmochim. Ac.*, 64, 1013–1027, 2000.
- Hruska, J.: Contribution of natural organic acids to surface waters acidity in wetland areas affected by anthropogenic acidification. Ph.D. Thesis, Czech Geological Survey, Prague, 86 pp., 1994.
- IPCC: Climate Change 2007 Synthesis Report, Contribution of Working Groups I, II and III to the Fourth assessment report of the Intergovernmental Panel on Climate Change, Core Writing Team, edited by: Pachauri, R. K. and Reisinger, A., IPCC, Geneva, Switzerland 104 pp., 2007.
- Jedrysek, M. O. and Skrzypek, G.: Hydrogen, carbon and sulfur isotope ratios in peat: The role of diagenesis and water regimes in reconstruction of past climates, *Environ. Chem. Lett.*, 2, 179–183, 2005.
- Johnson, L. C. and Damman, A. W. H.: Species-controlled *Sphagnum* decay in a south Swedish raised bog, *Oikos*, 61, 234–242, 1991.
- Keller J. K. and Bridgham, S. D.: Pathways of anaerobic carbon cycling across an ombrotrophic-minerotrophic peatland gradient, *Limnol. Oceanogr.*, 52, 96–105, 2007.
- Knorr, K.-H., Glaser, B., and Blodau, C.: Fluxes and <sup>13</sup>C isotopic composition of dissolved carbon and pathways of methanogenesis in a fen soil exposed to experimental drought, *Biogeochemistry*, 5, 1457–1473, 2008, <http://www.biogeosciences.net/5/1457/2008/>.
- Laird, N. M. and Ware, J. H.: Random-effects models for longitudinal data, *Biometrics*, 38, 963–974, 1982.
- Lamers, L. P. M., Falla, S. J., Sambprska, E. M., van Dulken, L. A. R., van Hengstum, G., and Roelofs, J. G. M.: Factors controlling the extent of eutrophication and toxicity in sulfate-polluted freshwater wetlands, *Limnol. Oceanogr.*, 47, 585–593, 2002.
- Lansdown, J. M., Quay, P. D. and Kingl, S. L.: CH<sub>4</sub> production via CO<sub>2</sub> reduction in a temperate bog – a source of <sup>13</sup>C-depleted CH<sub>4</sub>, *Geochim. Cosmochim. Ac.*, 56, 3493–3503, 1992.
- Limpens, J. and Berendse, F.: How litter quality affects mass loss and N loss from decomposing *Sphagnum*, *Oikos*, 103, 537–547, 2003.
- Loader, N. J., McCarroll, D., Van der Knaap, W. O., Robertson, I., and Gagen, M.: Characterizing carbon isotopic variability in *Sphagnum*, *Holocene*, 17, 403–410, 2007.
- Mikaloff Fletcher, S. E., Tans, P. P., Bruhwiler, L. M., Miller, J. B., and Heimann, M.: CH<sub>4</sub> sources estimated from atmospheric observations of CH<sub>4</sub> and its <sup>13</sup>C/<sup>12</sup>C isotopic ratios: 1. Inverse modelling of source processes, *Global Biogeochem. Cy.*, 18, GB4004, doi:10.1029/2004GB002223, 2004.
- Moore, T. R., Roulet, N. T., and Waddington, J. M.: Uncertainty in predicting the effect of climatic change on the carbon cycling of Canadian peatlands, *Climatic Change*, 40, 229–245, 1998.
- Mulligan, R. C. and Gignac, L. D.: Bryophyte community structure in a boreal poor fen: Reciprocal transplants, *Can. J. Botany – Rev. Can. Botanique*, 79, 404–411, 2001.
- Nadelhoffer, K. J. and Fry, B.: Controls on natural nitrogen-15 and carbon-13 abundances in forest soil organic matter, *Soil Sci. Soc. Am. J.*, 52, 1633–1640, 1988.
- Novak, M., Bottrell, S. H., Fottova, D., Buzek, F., Groscheova, H.,

- and Zak, K.: Sulfur isotope signals in forest soils of Central Europe along an air-pollution gradient, *Environ. Sci. Technol.*, 30, 3473–3476, 1996.
- Novak, M., Brizova, E., Adamova, M., Erbanova, L., and Bottrell, S. H.: Accumulation of organic carbon over the past 150 years in five freshwater peatlands in western and central Europe, *Sci. Total Environ.* 390, 426–436, 2008.
- Novak, M., Buzek, F., and Adamova, M.: Vertical trends in  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{34}\text{S}$  ratios in bulk *Sphagnum* peat, *Soil Biol. Biochem.*, 31, 1343–1346, 1999.
- Novak, M., Buzek, F., Harrison, A. F., Prechova, E., Jackova, I., and Fottova D.: Similarity between C, N and S stable isotope profiles in European spruce forest soils: Implications for the use of  $\delta^{34}\text{S}$  as a tracer, *Appl. Geochem.*, 18, 765–779, 2003.
- Novak, M., Jackova, I., and Prechova, E.: Temporal trends in the isotope signature of air-borne sulfur in Central Europe, *Environ. Sci. Technol.*, 35, 255–260, 2001.
- Novak, M., Kirchner, J. W., Fottova, D., Prechova, E., Jackova, I., Kram, P., and Hruska, J.: Isotopic evidence for processes of sulfur retention/release in 13 forested catchments spanning a strong pollution gradient (Czech Republic, central Europe), *Global Biogeochem. Cy.*, 19, GB4012, doi:10.1029/2004GB002396, 2005.
- Novak, M., Wieder, R. K. and Schell, W. R.: Sulfur during early diagenesis in *Sphagnum* peat: Insights from  $\delta^{34}\text{S}$  ratio profiles in  $^{210}\text{Pb}$  dated peat cores, *Limnol. Oceanogr.*, 39, 1172–1185, 1994.
- R Development Core Team: R: A Language and Environment for Statistical Computing, available at: <http://www.R-project.org>, ISBN 3-900051-07-0, 2008.
- Rice, S. K.: Variation in carbon isotope discrimination within and among *Sphagnum* species in a temperate wetland, *Oecologia*, 123, 1–8, 2000.
- Skrzypek, G., Kaluzny, A., Wojtun, B. and Jedrysek, M. O.: The carbon stable isotopic composition of mosses: A record of temperature variation, *Organic Geochem.*, 38, 1770–1781, 2007.
- Sohlenius, B. and Bostrom, S.: Effects of global warming on nematode diversity in a Swedish tundra soil – a soil trasplantation experiment, *Nematology*, 1, 659–709, 1999.
- Steinmann, P., Eilrich, B., Leuenberger, M. and Burns, S. J.: Stable carbon isotope composition and concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  in the deep catotelm of a peat bog, *Geochim. Cosmochim. Ac.*, 72, 6015–6026, 2008.
- Turetsky, M. R., Manning, S. W. and Wieder, R. K.: Dating recent peat deposits, *Wetlands*, 24, 324–356, 2004.
- Turetsky, M. R. and Ripley, S.: Decomposition of extreme rich fens of boreal Alberta, Canada, *Soil Sci. Soc. Am. J.*, 69, 1856–1860, 2005.
- Updegraff, K., Bridgham, S. D., Pastor, J., Weishampel, P. and Harth, C.: Response of  $\text{CO}_2$  and  $\text{CH}_4$  emissions from peatlands to warming and water table manipulation, *Ecol. Appl.*, 11, 311–326, 2001.
- Urban, N. R., Eisenreich, S. J., Grigal, D. F., and Schurr, K. T.: Mobility and diagenesis of  $^{210}\text{Pb}$  in peat, *Geochim. Cosmochim. Ac.*, 54, 1516–1534, 1990.
- Vile, M. A., Bridgham, S. D., and Wieder, R. K.: Response of anaerobic carbon mineralization rates to sulfate amendments in a boreal peatland, *Ecol. Appl.*, 13, 720–734, 2003.
- Vile, M. A., Wieder, R. K., and Novak, M.: Mobility of Pb in *Sphagnum*-derived peat, *Biogeochemistry*, 45, 35–52, 1999.
- Vile, M. A., Wieder, R. K., and Novak, M.: 200 years of Pb deposition throughout the Czech Republic: Patterns & sources, *Environ. Sci. Technol.*, 34, 12–21, 2000.
- Vitt, D. H., Wieder, R. K., Halsey, L. A., and Turetsky, M. R.: Response of *Sphagnum fuscum* to nitrogen deposition: A case study of ombrogenous peatlands in Alberta, Canada, *Bryologist*, 106, 235–245, 2003.
- Westbrook, C. J., Devito, K. J., and Allan, C. J.: Soil N cycling in harvested and pristine boreal forests and peatlands, *Forest Ecol. Management*, 234, 227–237, 2006.
- Whiticar, M. J.: Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, *Chem. Geol.*, 161, 291–314, 1999.
- Wieder, R. K., Novak, M., Schell, W. R. and Rhodes, T.: Rates of peat accumulation over the past 200 years in five *Sphagnum*-dominated peatlands in the United States, *J. Paleolimnol.*, 12, 35–47, 1994.
- Wieder, R. K. and Vitt, D. H.: *Boreal Peatland Ecosystems*, Ecological Studies 188, Springer-Verlag Berlin Heidelberg, 444 pp., 2006.
- Wieder, R. K. and Yavitt, J. B.: Peatlands and global climate change: Insights from comparative studies situated along a latitudinal gradient, *Wetlands*, 14, 229–238, 1994.
- Woodwell, G. M., Mackenzie, F. T., Houghton, R. A., Apps, M. J., Gorham, E. and Davidson, E. A.: Will the warming feed the warming?, in: *Biotic Feedbacks in the Global Climatic System*, edited by: Woodwell, G. M. and Mackenzie, F. T., 393–411, Oxford University Press, New York, 1995.
- Wynn, J. G., Harden J. W., and Fries T. L.: Stable carbon isotope depth profiles and soil organic carbon dynamics in the lower Mississippi Basin, *Geoderma*, 131, 89–109, 2006.
- Yavitt, J. B., Williams, C. J. and Wieder, R. K.: Controls on microbial production of methane and carbon dioxide in three *Sphagnum*-dominated peatland ecosystems as revealed by a reciprocal peat transplant experiment, *Geomicrobiol. J.*, 17, 61–68, 2000.
- Yavitt, J. B., Williams, C. J., and Wieder, R. K.: Soil chemistry versus environmental controls on production of  $\text{CH}_4$  and  $\text{CO}_2$  in northern peatlands, *Eur. J. Soil Sci.*, 56, 169–178, 2005.
- Yu, Z., Turetsky, M. R., Campbell, I. D., and Vitt, D. H.: Modelling long-term peatland dynamics. II. Processes and rates as inferred from litter and peat-core data, *Ecol. Model.*, 145, 159–173, 2001.