

# Stable carbon isotopes as indicators for environmental change in palsa peats

C. Alewell<sup>1</sup>, R. Giesler<sup>2</sup>, J. Klaminder<sup>2</sup>, J. Leifeld<sup>3</sup>, and M. Rollog<sup>1</sup>

<sup>1</sup>Institute of Environmental Geosciences, University of Basel, Switzerland

<sup>2</sup>Climate Impacts Research Centre, Dept. of Ecology and Environmental Science, Umeå University, Abisko, Sweden

<sup>3</sup>Agroscope Reckenholz-Tänikon Research Station ART, Switzerland

Received: 27 December 2010 – Published in Biogeosciences Discuss.: 19 January 2011

Revised: 20 June 2011 – Accepted: 20 June 2011 – Published: 8 July 2011

**Abstract.** Palsa peats are unique northern ecosystems formed under an arctic climate and characterized by a high biodiversity and sensitive ecology. The stability of the paltas are seriously threatened by climate warming which will change the permafrost dynamic and induce a degradation of the mires.

We used stable carbon isotope depth profile in two palsa mires of Northern Sweden to track environmental change during the formation of the mires. Soils dominated by aerobic degradation can be expected to have a clear increase of carbon isotopes ( $\delta^{13}\text{C}$ ) with depth, due to preferential release of  $^{12}\text{C}$  during aerobic mineralization. In soils with suppressed degradation due to anoxic conditions, stable carbon isotope depth profiles are either more or less uniform indicating no or very low degradation or depth profile turn to lighter values due to an enrichment of recalcitrant organic substances during anaerobic mineralisation which are depleted in  $^{13}\text{C}$ .

The isotope depth profile of the peat in the water saturated depressions (hollows) at the yet undisturbed mire Storfla et indicated very low to no degradation but increased rates of anaerobic degradation at the Stordalen site. The latter might be induced by degradation of the permafrost cores in the uplifted areas (hummocks) and subsequent breaking and submerging of the hummock peat into the hollows due to climate warming. Carbon isotope depth profile of hummocks indicated a turn from aerobic mineralisation to anaerobic

degradation at a peat depth between 4 and 25 cm. The age of these turning points was  $^{14}\text{C}$  dated between 150 and 670 yr and could thus not be caused by anthropogenically induced climate change. We found the uplifting of the hummocks due to permafrost heave the most likely explanation for our findings. We thus concluded that differences in carbon isotope profile of the hollows might point to the disturbance of the mires due to climate warming or due to differences in hydrology. The characteristic profiles of the hummocks are indicators for micro-geomorphic change during permafrost up heaving.

## 1 Introduction

Global climate change is significantly threatening stability and functioning of permafrost soils in extended areas of the northern latitudes and/or at high altitudes (Luoto et al., 2004; Brown and Romanowsky, 2008). A thawing of permafrost soils will most likely result in a positive feedback mechanism due to accelerated degradation of soil organic matter (Schuur et al., 2009; Dorrepaal et al., 2009). Furthermore, biodiversity and functioning of these unique ecosystems are under immediate threat (Luoto et al., 2004). One very unique northern ecosystem type are palsa peats, also called palsa mires. Palsa mires are a type of peat land typified by characteristic high mounds (called palsa or palsa *hummocks*), each with a permanently frozen core. Cryoturbation induces formation of the hummocks, where the volumetric expansion following freezing of the underlying horizons uplift the peat out of the groundwater saturated zone (Vasil'chuk et al., 2002;



Correspondence to: C. Alewell  
(christine.alewell@unibas.ch)

2003). Between the hummocks are wet depressions (called *hollows*), where permafrost is less extensive or absent. Palsa mires are common in high-latitude areas across the northern hemisphere including the northern parts of Scandinavia and characterized by a unique geochemistry and biodiversity (Railton and Sparling, 1973; Masing et al., 2010). Hydrology and vegetation composition as well as degradation and mineralisation patterns will change in these sensitive ecosystems because they are currently exposed to climate change (Åkerman and Johansson, 2008; Lemke et al., 2007). The latter should be reflected in stable carbon isotope depth patterns of the peat horizons.

The depth distribution of stable carbon isotopes ( $^{12}\text{C}$  and  $^{13}\text{C}$ ) reflect the combined effects of plant fractionation processes and microbial decomposition (Krull and Retallack, 2000). The fractionation within the plant towards slowly decomposing substances depleted in  $^{13}\text{C}$  and more easily degradable material relatively enriched in  $^{13}\text{C}$  leads to a depletion of  $^{13}\text{C}$  in the remaining, recalcitrant organic matter in the soil litter (Ågren et al., 1996). In contrast, the preferential respiration of  $^{12}\text{C}$  from decomposers may lead to an enrichment of  $^{13}\text{C}$  in the remaining soil organic matter (Ågren et al., 1996; Nadelhoffer and Fry, 1988). The balance between the latter two mechanisms will shape the carbon isotope depth profile in soils, which then reflect the dominating fractionation mechanism.

The aim of this study was to use stable carbon isotope depth profile in northern palsa peat complexes as indicators of environmental change and/or soil forming processes in space and time. Our hypothesis was that (i) hummocks and hollows should differ significantly in their stable isotope depth profile and (ii) that vertical trends reflect hydrological and botanical conditions mainly controlling decomposition processes at the time when the peat was deposited.

## 2 Theoretical concepts to interpret $\delta^{13}\text{C}$ C depth profile in soils

Isotopic depth profile in soils, which are not influenced by a change from C3 to C4 plants or by major changes in species composition have been reported as three different trends (Fig. 1):

### 2.1 Uniform or slightly increasing depth trend in the $\delta^{13}\text{C}$

A uniform or only slightly increasing depth trend in the carbon isotopic signature of bulk soils can be found in relatively young and/or poorly drained soils with little time for soil formation, and/or limited decomposition and thus limited fractionation (Fig. 1a). Several studies found uniform depth trends in water saturated peats with little or no fractionation of  $\delta^{13}\text{C}$  (Kracht and Gleixner, 2000; Clymo and Bryant, 2008; Skrzypek et al., 2008). Clymo and Bryant (2008)

showed that  $\delta^{13}\text{C}$  of a 7 m deep Scottish bog was rather uniform because opposite fractionation effects of  $\text{CO}_2$  and  $\text{CH}_4$  formation resulted in similar  $\delta^{13}\text{C}$  signatures of degradation product and sources (relative enrichment and depletion relative to source material, respectively). Thus, anaerobic decay with methane production, which requires low redox potential under anaerobic conditions (e.g., acetate fermentation) might also result in uniform  $\delta^{13}\text{C}$  depth profiles

### 2.2 A $\delta^{13}\text{C}$ depth trend towards slightly lower values

Trends in carbon isotope depth profile towards slightly lower values are common for soils that are constantly waterlogged such as peat-producing histosols (Fig. 1b; Krull and Retallack, 2000) but have significant anaerobic degradation. The slight decrease in  $\delta^{13}\text{C}$  is due to preservation of slowly decomposing  $^{13}\text{C}$  depleted substances like lignin (Benner et al., 1987). Since Sphagnum species have phenolic compounds very similar to lignin (Nimz and Tutschek, 1977; Rasmussen et al., 1995; Farmer and Morrison, 1964), a similar fractionation pattern can be expected in sphagnum peats. Thus, if we see a depth trend towards lower  $\delta^{13}\text{C}$  values this indicates an environment, where the enrichment of recalcitrant material dominates the isotopic profile

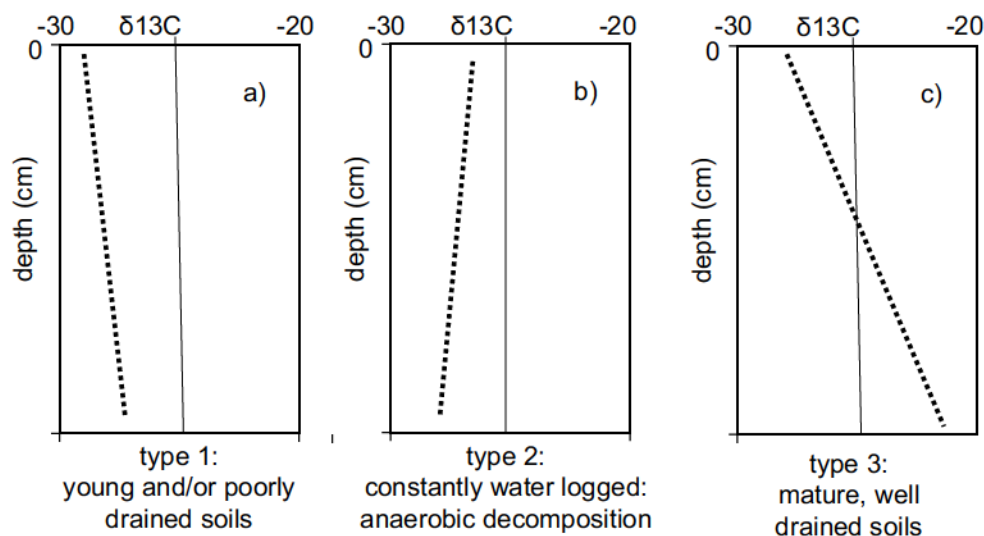
### 2.3 Pronounced $\delta^{13}\text{C}$ increases with depth of up to 5 ‰

Pronounced  $\delta^{13}\text{C}$  increases with depth of up to 5 ‰ are typical for mature, well drained soils, because aerobic decomposition favours selective loss of  $^{12}\text{C}$  (Fig. 1c; Nadelhoffer and Fry, 1988; Beckerheidmann and Scharpenseel, 1989; Ågren et al., 1996). Clay minerals in deeper soil horizons also favour this pattern in preferentially adsorbing the heavier  $^{13}\text{C}$  (Beckerheidmann and Scharpenseel, 1986), but the latter effect should be negligible in the peats we investigate in this study.

## 3 Site description

The two studied sites, Storfla et (68°20'51" N, 18°15'55" E) and the eastern Stordalen mire (68°20'90" N, 18°58'57" E) are situated about 3 km apart within a large palsa peat complex in the Abisko valley, northern Sweden. Storfla et is characterized by a stable palsa plateau with a fairly homogeneous thickness of about 0.5 m. The eastern Stordalen site is a partly degraded palsa system having an average peat depth around 0.5 m, but with large local variations. The thickness of the active layer, i.e. the seasonally thawing zone is in late September typically about 0.5 m in the hummocks and between 1 and 3 m in the hollows in both mires.

Permafrost heave drives the topography of the mires; higher uplifted palsa hummocks are typically situated between 1 to 3 m above the surrounding, less uplifted wetter areas. Hummocks are mainly dominated by nutrient poor vegetation such as dwarf shrubs (*Empetrum hemafraditum*, *Betula*



**Fig. 1.** Theoretical concept of isotope depth profiles in soils under regimes of differing metabolisms due to differences in water saturation and/or age.

*nana*), lichens (*Cladonia* spp.) and mosses (*Sphagnum fuscum*, *Dicranum elongatum*), indicating ombrotrophic conditions, i.e. a disconnection from the groundwater source. In the hollows formed beneath the hummocks common plants are *Carex rostrata* and *Eriophorum angustifolium* indicating groundwater inputs of nutrients and thus minerotrophic conditions (Malmer et al., 2005).

The depth of the active layer has been monitored in the Abisko valley since 1978. This monitoring shows an average increase in the active layer between 1978 to 2006 by about  $1 \text{ cm yr}^{-1}$  and a recent phase (since the mid-1990) of accelerated thawing (Åkerman and Johansson, 2008). In the time between 1970 and 2000 a large expansion of wet fen communities has been documented in Stordalen (Malmer et al., 2005) but not in Storflaket (Åkerman and Johansson, 2008), making the latter mire more representative of an un-degraded palsas system.

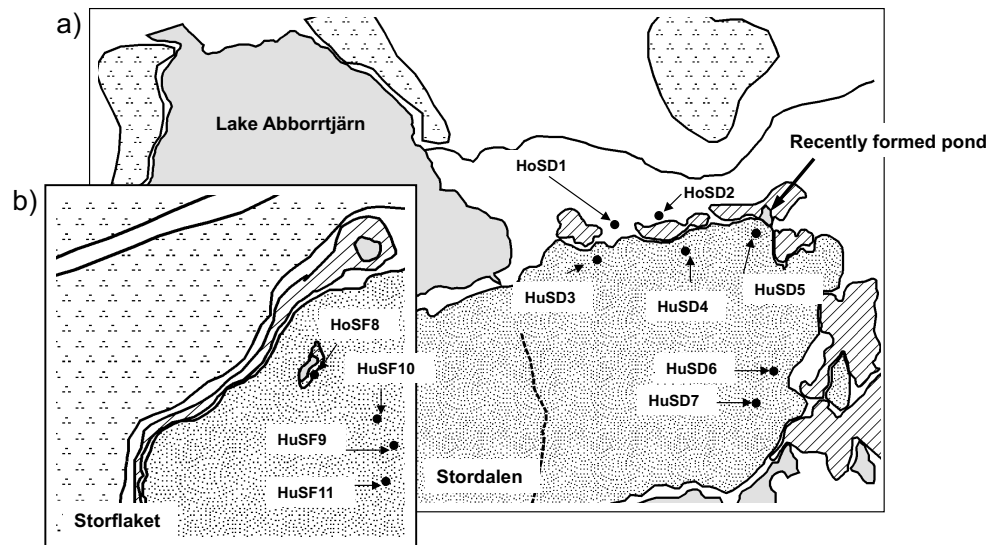
#### 4 Methods

Peat cores were taken in September 2007 at seven sites with 4 cores each at the Storflaket and the Stordalen mire representing stable hummocks ( $n = 4$ ) and hollow peat ( $n = 3$ ). Peat cores were collected using a Wardenaar peat corer (Wardenaar, 1987) for the upper  $\sim 0.5 \text{ m}$  and a Russian peat corer for deeper peat layers. The peat cores were cut in the field in 0.01 to 0.05 m sections and stored in air tight plastic bags. A re-sampling of the mires was done in June 2009 for two of the hollows (HoSD1, HoSD2), because core sections where either not distributed evenly or no sample material was left over for stable isotope analysis. Additionally, five palsas hummock profiles (HuSD6, HuSD7, HuSF10, HuSF11) where

sampled close to the former locations of HuSD5 and HuSF9, respectively, to validate the isotope patterns of the 2007 samples. For location of the sampled profiles please see the map in Fig. 2.

Stable carbon isotope analyses were accomplished using a continuous flow isotope ratio mass spectrometer (DELTA<sup>plus</sup> XP, Thermo Finnigan, Bremen, Germany) coupled with a FLASH Elemental Analyzer 1112 (Thermo Finnigan, Milan, Italy) combined with a CONFLO III Interface (Thermo Finnigan, Bremen, Germany) following standard processing techniques. Stable isotope ratios are reported as  $\delta^{13}\text{C}$  values [‰] relative to V-PDB defined in terms of NBS 19 = 1.95 ‰. The long term reproducibility for all standards is better than 0.1 ‰.

C-14 was measured at the Radiocarbon Laboratory of the University of Arizona following the method of Polach et al. (1973). Samples were treated with 1N HCl to remove carbonate, then with 2 % NaOH solution to remove any alkali-soluble organic carbon fraction. Finally, samples were rinsed with very dilute HCl until the sample pH was about 5. The residual sample was dried, and then combusted in a stream of pure oxygen gas. The resultant  $\text{CO}_2$  was purified by passage through cryogenic and chemical traps. It was reacted with Li metal at  $500^\circ\text{C}$  to produce  $\text{Li}_2\text{C}_2$ . The  $\text{Li}_2\text{C}_2$  was reacted with water at room temperature to yield  $\text{C}_2\text{H}_2$  gas, which was trimerized on a  $\text{Cr}^{6+}$  catalyst to give benzene. The benzene was stripped from the catalyst at approx.  $+80^\circ\text{C}$  and diluted to 3 g if necessary with pure benzene of petrochemical origin, containing no radiocarbon. Three mL of benzene was mixed with butyl-PBD scintillant, and radioactive decays were counted in a liquid scintillation spectrophotometer. (We use 2 Quantulus 1220 Spectrometers and a Wallac Rackbeta Spectrometer).



**Fig. 2.** Map showing the coring sites at (a) Stordalen and (b) Storfla et mires. Cores are labelled Ho = Hollow, Hu = Hummock, SD = Stordalen, SF = Storfla et and in ascending order from 1 to 11 according to the sampling sequence.

Figure 2

The bomb  $^{14}\text{C}$  model from Harkness et al. (1986) was used to calculate mean residence times (MRTs) of the bulk soil (for a detailed description of the model calculation see Leifeld and Fuhrer, 2009).

Peat accumulation rates have been calculated from  $\text{C}^{14}$  MRTs in the respective depth of samples.

Regression analysis was carried out with the software package SPSS from PASWStatistics18.0.

## 5 Results and discussion:

### 5.1 Isotope depth profile in the hummocks

Six out of eight investigated hummocks show a very clear pattern: an increase of  $\delta^{13}\text{C}$  isotope profile down to a certain depth (called here “turning points”) and then a decrease to lighter values in the deeper horizons (Fig. 3). A regression analysis resulted in significant negative slopes (increasing  $\delta^{13}\text{C}$ ) for the upper part of the profile above the turning point and significant positive slopes (decreasing  $\delta^{13}\text{C}$ ) below the turning points (Table 1, with the exception of HuSD6 in the upper and HuSD7 in the lower profiles where slope trends were not significant due to low sample numbers).

The increase in  $\delta^{13}\text{C}$  with depth down to the turning point is regardless of the peak depth always around  $\Delta^{13}\text{C} = 3.2 - 4\text{‰}$  (Table 2). The atmospheric composition of  $\text{CO}_2$  has decreased from  $\delta^{13}\text{C}$  values around  $-6.4\text{‰}$  at the end of the eighteenth century to values around  $-7.6\text{‰}$  in 1980 due to emissions from burning of fossil fuels, the so called Suess effect (Friedli et al., 1986). A further decrease to values of around  $-8.1\text{‰}$  in 2002 was measured by Keeling et al. (2005). If this decrease in  $\delta^{13}\text{C}$  of  $1.7\text{‰}$  over the last

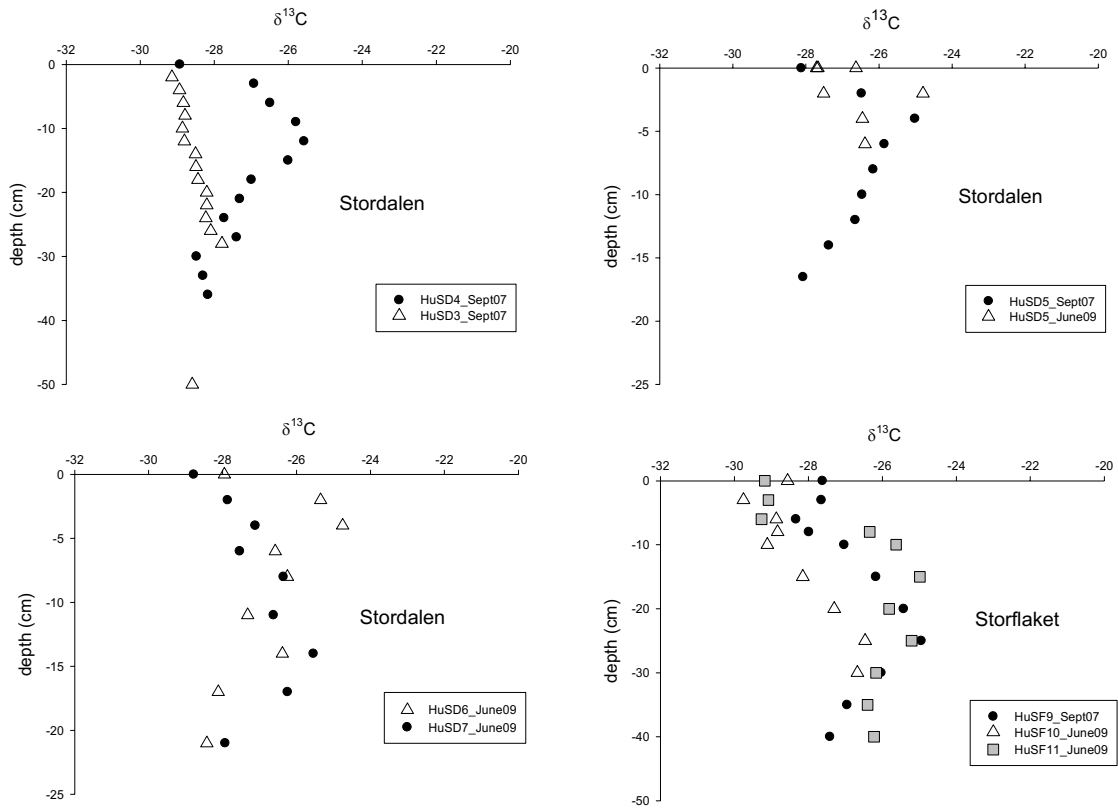
**Table 1.** Regression coefficient for the linear function depth =  $a + b \cdot \delta^{13}\text{C}$  in the investigated hummocks. up = above and low = below the turning points.

Site	Depth (cm)	<i>n</i>	<i>a</i>	<i>b</i>	<i>R</i> <sup>2</sup>
HuSD4	up $\geq -12$	5	-28.31	-0.26*	0.86
	low $\leq -12$	9	-24.62	+0.11****	0.85
HuSD5	up $\geq -4$	9	-27.45	-0.47*	0.44
	low $\leq -4$	9	-24.99	+0.17**	0.75
HuSD6	up $\geq -4$	3	-27.62	-0.80 <sup>n.s.</sup>	0.88
	low $\leq -4$	7	-24.79	+0.18*	0.75
HuSD7	up $\geq -14$	7	-28.40	-0.20**	0.87
	low $\leq -14$	3	-20.58	+0.35 <sup>n.s.</sup>	0.98
HuSF9	up $\geq -25$	8	-28.34	-0.13**	0.83
	low $\leq -25$	4	-20.93	+0.17*	0.97
HuSF11	up $\geq -15$	6	-29.75	-0.33*	0.80
	low $\leq -15$	6	-24.40	+0.05*	0.67

\*  $p < 0.05$ , \*\*  $p < 0.01$ , \*\*\*  $p < 0.001$ , \*\*\*\*  $p < 0.0001$ , n.s. = not significant

150 yr plays a crucial role for the  $\delta^{13}\text{C}$  of peats, it will only be documented in the upper cm of the peat because of the high soil age of up to several hundreds/ thousands of years. In an investigation of wetland soils in the Swiss Alps (Urseren Valley, Kanton Uri; Schaub and Alewell, 2009) no considerable increase of  $\delta^{13}\text{C}$  with depth was detected. However, depending on soil age a slight increase in  $\delta^{13}\text{C}$  with depth due to the Suess effect might be possible in wetland soils. The increase with depth in the upper horizons of the investigated peat mires can not be explained by the Suess effect, since this would only correspond to an increase of approximately  $1.7\text{‰}$ . Furthermore, the Suess effect should have occurred

## Hummocks



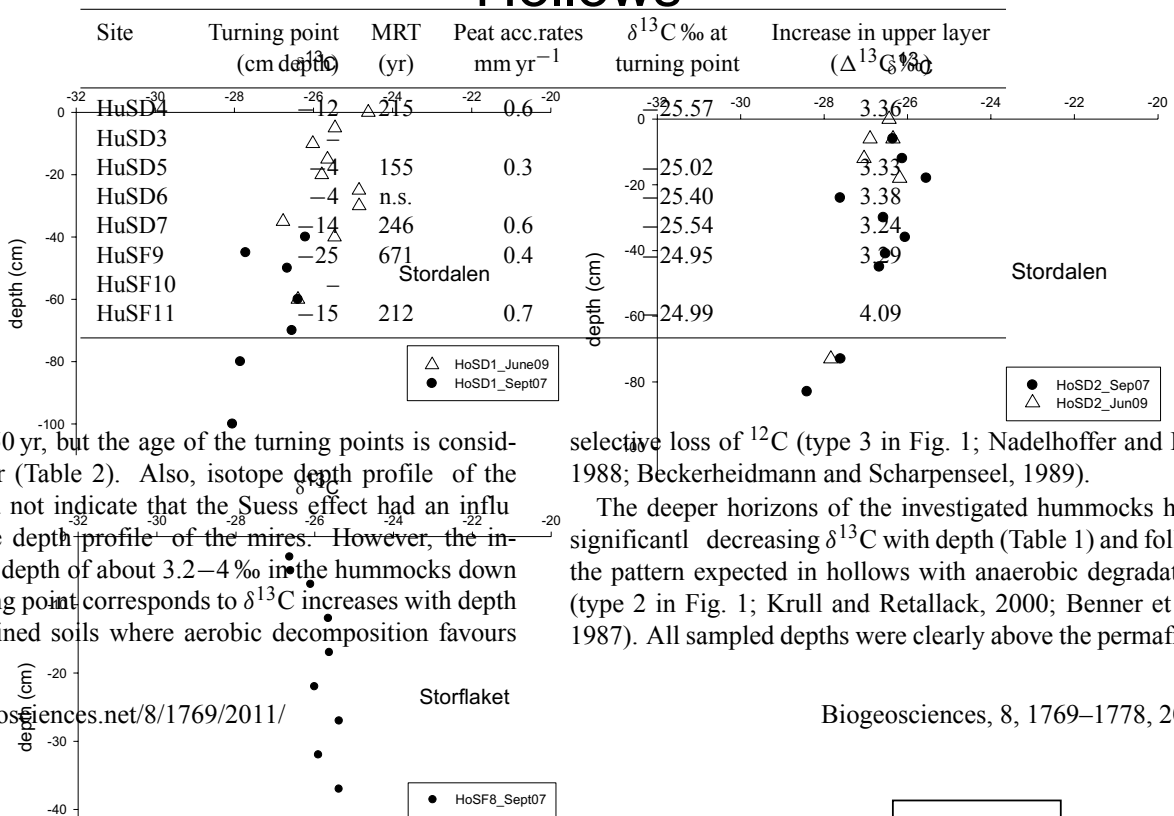
572

**Fig. 3.** Isotope depth profile of the investigated hummocks.  $\delta^{13}\text{C}$  in ‰.

573

**Table 2.** Turning points,  $\text{C}^{14}$  ages at turning point as mean residence time in years (MRT), peat accumulation rates per year, stable carbon isotope value of the turning point and the increase in stable carbon isotopes in the upper layer ( $\Delta^{13}\text{C}$ ). n.s. = Harkness et al. (1986) model unsolvable.

## Hollows



in the last 50 yr, but the age of the turning points is considerably older (Table 2). Also, isotope depth profile of the hollows did not indicate that the Suess effect had an influence on the depth profile of the mires. However, the increase with depth of about 3.2–4 ‰ in the hummocks down to the turning point corresponds to  $\delta^{13}\text{C}$  increases with depth of well drained soils where aerobic decomposition favours

selective loss of  $^{12}\text{C}$  (type 3 in Fig. 1; Nadelhoffer and Fry, 1988; Beckerheidmann and Scharpenseel, 1989).

The deeper horizons of the investigated hummocks have significantly decreasing  $\delta^{13}\text{C}$  with depth (Table 1) and follow the pattern expected in hollows with anaerobic degradation (type 2 in Fig. 1; Krull and Retallack, 2000; Benner et al., 1987). All sampled depths were clearly above the permafrost

layer and well within the active layer and none of the hummock samples were from a permanently water saturated horizon. The stable isotope profile might indicate that at a certain point in time the metabolism changed from anaerobic to aerobic degradation. The most likely explanation for this change would be a form of cryoturbation where the permafrost lifted hollow peat material out of the groundwater level zone. Even though the palsas hummocks are formed by cryoturbation, age inversions of the peat seem to be practically absent during this process (Vasil'chuk et al., 2002, 2003). It is important to consider that 80–90 % of organic matter decomposition in bogs takes place in the Acrotelm (Clymo, 1984; Zaccone et al., 2008). Thus, the turning point may represent a situation where anaerobic decomposition with selective preservation of lignin or phenolic compounds is replaced by more aerobic degradation with the corresponding shift in  $\delta^{13}\text{C}$  of the bulk peat material (change from type 2 to type 3 depth pattern). Even if the herbaceous species contain only small amounts of lignin it may make up the vast majority of organic matter below the turning point because of selective preservation. Loisel et al. (2009) determined similar patterns in boreal hummocks and Zaccone et al. (2008) for the preservation of phenolic compounds in temperate ombrotrophic mountainous peats.

Samples representing the turning point were age dated with  $^{14}\text{C}$  radiocarbon dating. MRTs range from 155 yr at 4 cm depth at the Stordalen mire, to 670 yr in 25 cm depth at the Storflaet mire (Table 2). Thus, if the turning points in the isotope depth profile indicate environmental change or any kind of disturbance, this happened not at a large regional but rather at a small local scale at different points in time. MRTs indicate relatively homogenous peat accumulation rates in both mires between 0.3. and 0.6 mm yr<sup>-1</sup>.

## 5.2 Consideration of other possible influence on the turning points in the hummocks

The most plausible cause for the turning points in the isotope depth profile of the hummocks is an uplifting of the palsa during cryoturbation. However, isotope depth profile of bulk soils can be influenced by other driving factors, which we will discuss in the following.

### 5.2.1 Preferential leachate of relatively young organic substances

Other studies have observed a 1–3 ‰ return of the  $\delta^{13}\text{C}$  depth profile to more negative values in the lower B and C-horizon of mineral soils. The latter has been explained with a chromatographic-like effect with lower clay content in the deeper soil layers and thus a greater percentage of relatively young, and undecomposed organic substances, which leached down the soil profile compared to clay rich horizons with older, decomposed organo-mineral complexes (Beckerheidmann and Scharpenseel, 1989). The leaching of organic

substances down the profile is called podsolization in mineral soils. However, we investigated peat soils with a percentage of organic substance mostly >80 % in all horizons. Thus, a leaching of a few percent organic substances down the profile should hardly influence bulk  $\delta^{13}\text{C}$  of deeper horizons in our peats to such an extent.

### 5.2.2 Influence of methane and melting of permafrost

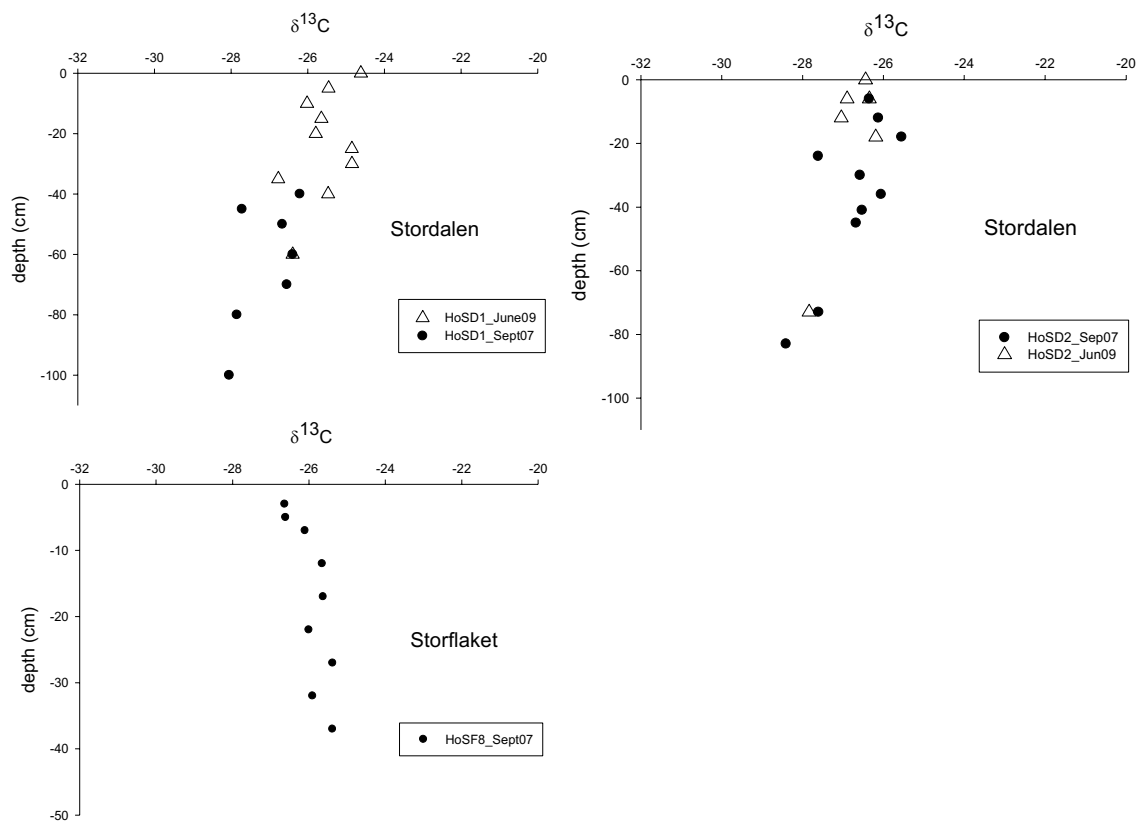
Rask and Schoenau (1993) have stated that a  $\delta^{13}\text{C}$  enrichment with depth or in space might not only point to aerobic mineralisation but also to times/zones with strong CH<sub>4</sub> production. The latter will lead to a preferential release of the light  $^{12}\text{CH}_4$  and an enrichment in the remaining organic matter (basically the same effect but stronger signals as aerobic mineralisation). However, increased methane release and subsequent methane oxidation (methanotrophy) can also lead to recycling of light  $^{12}\text{CO}_2$  and a shift to lighter values in the resulting organic material (Krull, 1999; Krull and Retallack, 2000; Krull et al., 2000). Increased methane release has been attributed to melting of permafrost in depth profiles of paleosols (Krull et al., 2000). Overall we would not expect CH<sub>4</sub> production or recycling to produce such consistent patterns in the depth profile but a much greater scattering of the  $\delta^{13}\text{C}$  data. However, some of the variances in the  $\delta^{13}\text{C}$  data might be due to this effect.

### 5.2.3 Change in vegetation

Carbon isotopes of ombrotrophic peat bog plants differ between species. This species effect can range from  $\delta^{13}\text{C} = -30$  ‰ for *Calluna* species to  $-22$  ‰ for *Sphagnum* (Menot and Burns, 2001) and has been determined for Arctic environments between  $-20$  ‰ (mosses) and  $-29$  ‰ (*Carex* species; Skrzypek et al., 2008). Thus, a change in species composition could theoretically explain all observed changes in our depth profile if we would assume major long term and gradual changes in vegetation. The maximal variation in  $\delta^{13}\text{C}$  values seen between hummocks and hollows at our sites range between  $-24.6$  to  $-29.2$  ‰ (Figs. 3 and 4). The average  $\delta^{13}\text{C}$  value of today's living vegetation at our sites is  $-25.9 \pm 1.1$  ‰ in the hollows and  $-28.2 \pm 0.8$  ‰ in the hummocks. Thus, a change from fen hollow peat towards ombrotrophic hummock peat with time can be expected to generate decreasing  $\delta^{13}\text{C}$  value in the younger hummock material. The latter would result in a similar depth pattern as aerobic mineralisation: relatively lighter  $\delta^{13}\text{C}$  values in the upper horizons and an increase with depth (type 3, Fig. 1).

Changes in vegetation would occur due to (a) changes in hydrology (e.g. uplifting of the palsas, submerging by erosion) or (b) through dramatic climatic change. The latter is not very likely because the turning points are (i) pretty sharp (meaning within a few cm of the profile and thus within a few decades) and (ii) quite recent but before anthropogenically induced climate change started. Thus, we can rule out

## Hollows



574

**Fig. 4.** Isotope depth profile of the investigated hollows.  $\delta^{13}\text{C}$  in ‰.

major climatic induced vegetation changes being responsible for soil formation at the depth of the turning points. However, if cryoturbation induces geomorphic processes (palsa uplifting, thermocast erosion and submerge of material) this might result in a change in hydrology followed by a change in vegetation.

Previous investigations of the vegetation at the sites confirm our results. In Stordalen, peat hollow has been dominated by sphagnum communities since the onset of peat formation (Malmer and Wallen, 1996). However, the peat in the hummocks developed from a carex dominated fen peat with woody debris into a drier ombrotrophic peat with *Calluna* and *Sphagnum* (Malmer and Wallen, 1996; Kokfelt et al., 2010). Such vegetation change is expected to give rise to a depth trend similar to the type 3 trend in Fig. 1 and might thus explain the upper profile of the hummocks. As explained above such a vegetation change was most likely not induced by a change in climate but was due to permafrost uplifting and a change in hydrology.

**Table 3.** Regression coefficients for the function  $depth = a + b \cdot \delta^{13}\text{C}$  in the investigated hollows.

Site	<i>n</i>	<i>a</i>	<i>b</i>	<i>R</i> <sup>2</sup>
HoSD1	17	-25.01	+0.03****	0.62
HoSD2	16	-26.26	+0.02**	0.49
HoSF8	9	-26.44	-0.03*	0.57

\*  $p < 0.05$ , \*\*  $p < 0.01$ , \*\*\*  $p < 0.001$ , \*\*\*\*  $p < 0.0001$

### 5.2.4 Change in hydrology

A change in hydrology can change the carbon isotopic composition beyond the change of vegetation or the change from aerobic to anaerobic metabolism. Higher water table depth causes enrichment in  $\delta^{13}\text{C}$  because a water film on the leaves will act as diffusion barrier for  $\text{CO}_2$ . The latter will result in lower fractionation factors during  $\text{CO}_2$  uptake and thus a relative enrichment in the plants under high water saturation or vice versa a relative depletion under low water saturation (Price et al., 1997 for *Sphagnum*; Pancost et al., 2003 for

bulk peat with changes of +4‰ from dry to wet; Loisel et al., 2009). If a shift in hydrology is the explanation for the  $\delta^{13}\text{C}$  depth profile this would indicate an increase in water saturation up to the turning point and then a decrease again. Thus, considering this effect the turning point of  $\delta^{13}\text{C}$  in the hummocks would, even though for different reasons, indicate the same change in hydrology as discussed above: high or even increasing water saturation during the peat formation of the lower horizons and then, from the turning point upwards a decrease or lower water saturation during the peat formation in the upper horizons. This is also in agreement with the time period when the Stordalen mire is assumed to have turned ombrotrophic, likely due to permafrost-induced up-lift of the palsa features (Rydberg et al., 2010).

### 5.3 Isotope depth profile in the hollows

The  $\delta^{13}\text{C}$  profile of all investigated hollows (Fig. 4) are congruent with depth patterns reported previously for water-logged soils (Benner et al., 1987; Krull and Retallack, 2000).

A regression analysis of the stable carbon isotope depth profile of the hollows resulted in significantly different slopes for the type 1 hollow Storfla et (slightly negative slope, Table 3) compared to the type 2 hollows Stordalen (slightly positive slopes, Table 3).

The  $\delta^{13}\text{C}$  depth profile of the hollow at Storfla et (HoSF8) is only very slightly increasing with depth indicating slow and suppressed decomposition rates (Krull and Retallack, 2000). This profile would also be compatible with organic matter formation under the regime of methanogenesis (see above, Clymo and Bryant, 2008). The water table in Storfla et is closer to the peat surface in the hummocks than in Stordalen (Klaminder et al., 2008). Thus, oxygen supply can be supposed to be very limited in the hollows of Storfla et which would explain the stable isotope profile which indicates low degradation rates at low redox potential favouring processes like methanogenesis. Furthermore, Storfla et in general and the sites we sampled for this study specifically, were (based on observations in the field) not strongly affected by thawing of the permafrost and succeeding degradation of hummocks yet.

The  $\delta^{13}\text{C}$  profile of the hollows at Stordalen (HoSD1 and HoSD2) decrease significantly with depth towards lower values (Table 3), which is typical for decomposition under anaerobic conditions with the remaining recalcitrant organic substances dominating the  $\delta^{13}\text{C}$  signature (Ågren et al., 1996; Benner et al., 1987; Krull and Retallack, 2000). Thus, Stordalen hollows seem to have relatively higher decomposition rates favouring a stronger accumulation of  $^{13}\text{C}$  depleted compounds such as lignin or phenols and/or generally a higher redox regime where processes like methanogenesis play a minor role compared to the hollow profile sampled in Storfla et. Hollows at Stordalen seem seriously affected by thawing, breaking and submerging of peat chunks from hummocks at the edge to the bigger hollows (see also

Klaminder et al., 2008). The new supply of hummock peat material in the hollows might increase degradation processes in the hollows, thus explaining the different  $\delta^{13}\text{C}$  profile at Stordalen with relatively heavier values in the upper horizons and a slight decrease with depth.

## 6 Conclusions

It is very likely that we see the influence of permafrost thawing due to climate change in the  $\delta^{13}\text{C}$  depth profile of the hollows in Stordalen. However, the distinct  $\delta^{13}\text{C}$  patterns in the hummocks (e.g. the “turning points”) cannot be attributed to global climate change, because age of turning points is older than anthropogenically induced climate change. Further, age of turning points vary at a very small local scale. Thus, a geomorphic induced change in the hydrology of the mires, e.g. the uplifting of the palsa due to cryoturbation is a more likely explanation for the observed patterns. We thus conclude:

1. The difference in depth profile between hollows in Storfla et and Stordalen indicates the difference in site disturbance due to climate change.
2. The most likely explanation of the depth profile of the hummocks is a change in degradational metabolism induced by permafrost uplifting during cryoturbation. The latter induced a change in hydrology in the palsa hummocks (from wet to dry), which was followed by vegetation changes. Since the age of the turning points is roughly between 150 and 700 yr, there is no indication that anthropogenically induced climate change is responsible for this pattern in the hummocks.

*Acknowledgements.* We thank Chris Eastoe for radiocarbon dating (Radiocarbon Laboratory at University of Arizona, US). The Climate Impacts Research Center (CIRC, Umea University, Sweden) substantially supported this study. We thank two anonymous reviewers for valuable comments and discussion.

Edited by: T. Treude

## References

- Ågren, G. I., Bosatta, E., and Balesdent, J.: Isotope discrimination during decomposition of organic matter: A theoretical analysis, *Soil Sci. Soc. Am. J.*, 60, 1121–1126, 1996.
- Åkerman, H. J. and Johansson, M.: Thawing permafrost and thicker active layers in sub-arctic Sweden, *Permafrost Periglac.*, 19, 279–292, doi:10.1002/ppp.626, 2008.
- Beckerheidmann, P. and Scharpenseel, H. W.: Thin-Layer Delta-C-13 and De-14 Monitoring of Lessive Soil Profiles *Radiocarbon*, 28, 383–390, 1986.
- Beckerheidmann, P. and Scharpenseel, H. W.: Carbon Isotope Dynamics in Some Tropical Soils, *Radiocarbon*, 31, 672–679, 1989.



- Benner, R., Fogel, M. L., Sprague, E. K., and Hodson, R. E.: Depletion of C-13 in Lignin and Its Implications for Stable Carbon Isotope Studies, *Nature*, 329, 708–710, 1987.
- Brown, J. and Romanowsky, V. E.: Report from the International Permafrost Association: State of permafrost in the first decade of the 21st century, *Permafrost Periglac.*, 19, 255–260, 2008.
- Clymo, R. S.: The Limits to Peat Bog Growth, *Philos. Trans. R. Soc. Lond. Ser. B-Biol. Sci.*, 303, 605–654, 1984.
- 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. Acta*, 72, 2048–2066, doi:10.1016/j.gca.2008.01.032, 2008.
- Dorrepaal, E., Toet, S., van Lotestijin, R. S. P., Swart, E., van de Weg, M. J., Callaghan, T. V., and Aerts, R.: Carbon respiration from subsurface peat accelerated by climate warming in the subarctic, *Nature*, 460, 616–619, 2009.
- Farmer, V. C. and Morrison, R. I.: Lignin in Sphagnum and Phragmites and in Peats Derived from These Plants, *Geochim. Cosmochim. Acta*, 28, 1537–1546, 1964.
- Friedli, H., Lotscher, H., Oeschger, H., Siegenthaler, U., and Stauffer, B.: Ice Core Record of the C-13/C-12 Ratio of Atmospheric CO<sub>2</sub> in the Past 2 Centuries, *Nature*, 324, 237–238, 1986.
- Harkness, D. D., Harrison, A. F., and Bacon, P. J.: The Temporal Distribution of Bomb C-14 in a Forest Soil, *Radiocarbon*, 28, 328–337, 1986.
- Keeling, C., Bollenbach, A., and Whorf, T.: In Trends: A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy: Oak Ridge, TN, USA, 2005.
- Klaminder, J., Yoo, K., Rydberg, J., and Giesler, R.: An explorative study of mercury export from a thawing peat mire, *J. Geophys. Res.-Biogeosci.*, 113, 1–9, 2008.
- Kokfelt, U., Reuss, N., Struyf, E., Sonesson, M., Rundgren, M., Skog, G., Rosen, P., and Hammarlund, D.: Wetland development, permafrost history and nutrient cycling inferred from late Holocene peat and lake sediment records in subarctic Sweden, *J. Paleolimnol.*, 44, 327–342, doi:10.1007/s10933-010-9406-8, 2010.
- Kracht, O. and Gleixner, G.: Isotope analysis of pyrolysis products from Sphagnum peat and dissolved organic matter from bog water, *Org. Geochem.*, 31, 645–654, 2000.
- Krull, E. S.: Permian peat mires as paleoenvironmental proxies, *Palaios*, 14, 530–544, 1999.
- Krull, E. S. and Retallack, G. J.: delta C-13 depth profile from paleosols across the Permian-Triassic boundary: Evidence for methane release, *Geol. Soc. Am. Bull.*, 112, 1459–1472, 2000.
- Krull, E. S., Retallack, G. J., Campbell, H. J., and Lyon, G. L.: delta C-13(org) chemostratigraphy of the Permian-Triassic boundary in the Maitai Group, New Zealand: evidence for high-latitude methane release, *N. Z. J. Geol. Geophys.*, 43, 21–32, 2000.
- Leifeld, J. and Fuhrer, J.: Long-term management effects on soil organic matter in two cold, high-elevation grasslands: clues from fractionation and radiocarbon dating, *Eur. J. Soil Sci.*, 60, 230–239, doi:10.1111/j.1365-2389.2008.01111.x, 2009.
- Lemke, P., Ren, J., Alley, R. B., Allison, I., Carrasco, J., Flato, G., Fujii, Y., Kaser, G., Mote, P., Thomas, R. H., and Zhang, T.: Observations: Changes in snow, ice and frozen ground, in: *Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment, Report of the Intergovernmental Panel on Climate Change*, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA, 337–384, 2007.
- Loisel, J., Garneau, M., and Helie, J. F.: Modern Sphagnum delta C-13 signatures follow a surface moisture gradient in two boreal peat bogs, James Bay lowlands, Quebec, *J. Quat. Sci.*, 24, 209–214, doi:10.1002/jqs.1221, 2009.
- Luoto, M., Fronzek, S., and Zuidhoff, F. S.: Spatial modelling of peat mires in relation to climate in northern Europe, *Earth Surf. Process. Land.*, 29, 1373–1387, doi:10.1002/esp.1099, 2004.
- Malmer, N. and Wallen, B.: Peat formation and mass balance in subarctic ombrotrophic peatlands around Abisko, northern Scandinavia, *Ecol. Bull., Plant ecology in the subarctic Swedish Lapland*, 45, 79–92, 1996.
- Malmer, N., Johansson, T., Olsrud, M., and Christensen, T. R.: Vegetation, climatic changes and net carbon sequestration in a North-Scandinavian subarctic mire over 30 years, *Glob. Change Biol.*, 11, 1895–1909, doi:10.1111/j.1365-2486.2005.01042.x, 2005.
- Masing, V., Botch, M., and Laanelaid, A.: Mires of the former Soviet Union, *Wetl. Ecol. Manag.*, 18, 397–433, doi:10.1007/s11273-008-9130-6, 2010.
- Menot, G. and Burns, S. J.: Carbon isotopes in ombrogenic peat bog plants as climatic indicators: calibration from an altitudinal transect in Switzerland, *Org. Geochem.*, 32, 233–245, 2001.
- Nadelhoffer, K. F. and Fry, B.: Controls on Natural N-15 and C-13 Abundances in Forest Soil Organic-Matter, *Soil Sci. Soc. Am. J.*, 52, 1633–1640, 1988.
- Nimz, H. H. and Tutschek, R.: C-13 NMR-spectra of lignins, 7. on question of lignin content of mosses (sphagnum-magellanicum brid), *Holzforschung*, 31, 101–106, 1977.
- Pancost, R. D., Baas, M., van Geel, B., and Damste, J. S. S.: Response of an ombrotrophic bog to a regional climate event revealed by macrofossil, molecular and carbon isotopic data, *Holocene*, 13, 921–932, doi:10.1191/0959683603hl674rp, 2003.
- Polach, H., Gower, J., and Fraser, I.: Synthesis of high-purity benzene for radiocarbon dating, in: *Proceedings of the 8th International 14C Conference*, edited by: Rafter, T. A. and Grant-Taylor, T., Wellington, Roy. Soc. New Zealand, 1, B36–B49, 1973.
- Price, G. D., McKenzie, J. E., Pilcher, J. R., and Hoper, S. T.: Carbon-isotope variation in Sphagnum form hummock-hollow complexes: Implications for Holocene climate reconstruction, *Holocene*, 7, 229–233, 1997.
- Railton, J. B. and Sparling, J. H.: Preliminary Studies on Ecology of Peat Mounds in Northern Ontario, *Can. J. Bot.-Rev. Can. Bot.*, 51, 1037–1044, 1973.
- Rask, H. M. and Schoenau, J. J.: C-13 Natural-Abundance Variations in Carbonates and Organic-Carbon from Boreal Forest Wetlands, *Biogeochem.*, 22, 23–35, 1993.
- Rasmussen, S., Wolff, C., and Rudolph, H.: Compartmentalization of Phenolic Constituents in Sphagnum, *Phytochemistry*, 38, 35–39, 1995.
- Rydberg, J., Klaminder, J., Rosen, P., and Bindler, R.: Climate driven release of carbon and mercury from permafrost mires increases mercury loading to sub-arctic lakes *Sci. Total Environ.*, 408, 4778–4783, 2010.
- Schaub, M. and Alewell, C.: Stable carbon isotopes as an indicator for soil degradation in an alpine environment (Urseren Valley,

- Switzerland), *Rapid Commun. Mass Spectrom.*, 23, 1499–1507, doi:10.1002/rem.4030, 2009.
- Schuur, A. E. G., Vogel, J. G., Crummer, K. G., Lee, H., Sickman, J. O., and Osterkamp, T. E.: The effect of permafrost thaw on old carbon release and net carbon exchange from tundra, *Nature*, 459, 556–559, 2009.
- Skrzypek, G., Paul, D., and Wojtun, B.: Stable isotope composition of plants and peat from Arctic mire and geothermal area in Iceland, *Pol. Polar. Res.*, 29, 365–376, 2008.
- Vasil'chuk, Y. K., Vasil'chuk, A. C., Budantseva, N. A., Volkova, E. M., Sulerzhitsky, L. D., Chizhova, J. N., and Junner, H.: Radiocarbon Age and Holocene Dynamics of Palsa in the USA River Valley, *Dokl. Earth Sci.*, 384, 442–447, 2002.
- Vasil'chuk, Y. K., Vasil'chuk, A. C., Sulerzhitsky, L. D., Budantseva, N. A., Volkova, E. M., and Chizhova, J. N.: Radiocarbon Chronology of Palsa in the Bol'shaya Zemlya Tundra, *Dokl. Earth Sci.*, 393, 1160–1164, 2003.
- Wardenaar, E. C. P.: A new hand tool for cutting peat profiles *Can. J. Botany*, 65, 1772–1773, 1987.
- Zaccone, C., Said-Pullicino, D., Gigliotti, G., and Mi-ano, T. M.: Diagenetic trends in the phenolic constituents of Sphagnum-dominated peat and its corresponding humic acid fraction, *Org. Geochem.*, 39, 830–838, doi:10.1016/j.orggeochem.2008.04.018, 2008.