Biogeosciences Discuss., 8, 10543–10576, 2011
www.biogeosciences-discuss.net/8/10543/2011/
doi:10.5194/bgd-8-10543-2011

Biogeosciences Discussions

Peat decomposition records in three pristine ombrotrophic bogs in southern Patagonia

T. Broder[1], C. Blodau[1,3,*], H. Biester[2], and K. H. Knorr[1]

[1]Limnological Research Station and Dept. of Hydrology, University of Bayreuth, Germany
[2]Institute for Environmental Geology, TU-Braunschweig, Germany
[3]School of Environmental Sciences, University of Guelph, Canada
[*]now at: Hydrology Group, Institute of Landscape Ecology, FB 14 Geosciences, University of Münster, Germany

Received: 16 September 2011 – Accepted: 16 October 2011 – Published: 26 October 2011

Correspondence to: K. H. Knorr (kh.knorr@uni-bayreuth.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Ombrotrophic bogs in southern Patagonia have been examined with regard to paleoclimatic and geochemical research questions but knowledge about organic matter decomposition in these bogs is limited. Therefore, we examined peat humification with depth by Fourier Transformed Infrared (FTIR) measurements of solid peat, C/N ratio, and $\delta^{13}C$ and $\delta^{15}N$ isotope measurements in three bog sites. Peat decomposition generally increased with depth but distinct small scale variation probably caused by environmental changes occurred. C/N ratios varied mostly between 40 and 120 and were significantly correlated ($R^2 > 0.55$, $p < 0.01$) with FTIR-derived humification indices. The degree of decomposition was lowest at the site with the least sea spray input, while the peat was most decomposed at the driest site with highest sea spray deposition. Decomposition of peat was also advanced near ash layers. Values of $\delta^{13}C$ were 26.5 ± 2‰ in the peat and partly related to decomposition indices, while $\delta^{15}N$ in the peat varied around zero and did not consistently relate to any decomposition index. Concentrations of DOM partly related to C/N ratios, partly to FTIR derived indices. DOM was enriched in ^{13}C and in ^{15}N relative to the solid phase probably due to multiple microbial modifications and recycling of N in these N-poor environments. In summary, paleoclimatic signals may have influenced decomposition according to depth profiles of C/N ratios, $\delta^{13}C$ values, and FTIR spectra, but the study also suggests that decomposition was also influenced by ash layers, sea spray input and other site specific factors.

1 Introduction

Peatlands cover about 3 % of the earth's surface (Aselmann and Crutzen, 1989) and occur in three different regions: a northern (boreal), tropical and southern region. Southern peatlands, mostly in Patagonia, have accumulated 13 to 18 Pg C during the Holocene with an overall accumulation rate of 22 g C m^{-2} yr^{-1} and cover 45 000 km^2

BGD
8, 10543–10576, 2011

(Yu et al., 2010). Prevailing westerly winds bring unpolluted air masses from the Pacific Ocean resulting in low atmospheric nitrogen deposition in the region (Godoy et al., 2003). As ombrotrophic bogs receive nutrients by atmospheric depositions only, Patagonian bogs provide a reference system compared to more polluted northern bogs. Southern Patagonia peatlands have thus been frequently used as paleoclimate archives (e.g. McCulloch and Davies, 2001; Markgraf, 1993; Heusser et al., 2000) and for examination of halogen and mercury deposition records (Biester et al., 2003, 2004). The validity of such records partly depends on the decomposition patterns of organic matter but investigations of different, complementary proxies to address this issue are scarce for this region.

In temperate bogs the majority of organic matter is decomposed in the upper, unsaturated layer of peat, i.e. the acrotelm, and only 10–20 % of the litter mass reaches the underlying, water-saturated catotelm. Here, anaerobic decomposition proceeds at a rate of only ∼ 1 % or less of the rate in the acrotelm (Clymo, 1984; Frolking et al., 2001; Beer et al., 2008). Controls of decomposition rates are the plant community type (e.g. Bragazza et al., 2007), temperature (e.g. Bridgham et al., 1999) and water-level position and soil moisture (e.g. Laiho, 2006). The slow decomposition rates under permanent waterlogged conditions result from combined effects of limited oxygen diffusion into the saturated peat, the poorly decomposable litter of *Sphagnum* vegetation (e.g. Hogg, 1993), low temperatures and further constraints on the processes, such as enzymatic activities or thermodynamics (e.g. Freeman et al., 2001; Beer and Blodau, 2007).

Peatlands in southern Patagonia are exposed to sea spray due to strong westerly winds and their close proximity to the sea (Kleinebecker et al., 2008). Sea spray contains various soluble salts, among them basic cations, sulfate, and also halogens (Biester et al., 2004). The basic cations may have a generally fertilizing effect (Kleinebecker et al., 2008) and sulfate may be used as an electron acceptor for anaerobic respiration (Segers and Kengen, 1998). Thus, a stimulation of anaerobic respiration by sea spray input may be postulated. Retained halogens in the peat serve as an

BGD
8, 10543–10576, 2011

indicator for the extent of sea spray input in this regard (Biester et al., 2004). In Patagonia also ash layers from various volcanic eruptions in the past occur, which can have an additional stimulating effect on decomposition due to nutrient supply or release of electron acceptors during weathering and diagenesis of the ashes (Hotes et al., 2010).

While such potential influences on organic matter decomposition and humification patterns have been identified, their relative impact is unknown. In this study we attempted to address this research gap using several indicators of organic matter decomposition along the depositional record, i.e. C/N ratios of organic matter, Fourier Transform Infrared spectroscopy (FTIR) and content of stable ^{13}C and ^{15}N isotopes in the peat. C/N ratios of the organic material have been shown to relate to decomposition processes (e.g. Malmer and Holm, 1984) as microbial consumption of carbon- and hydrogen-rich organic substances results in a decreased abundance of carbon relative to nitrogen. In addition, relative nitrogen abundance increased during degradation, as mineralized nitrogen is mostly retained in microbial biomass (Damman, 1988). Therefore, the C/N ratio has been commonly used as indicator for the degree of decomposition, based on the relatively higher loss of N compared to C during decomposition and thus indicating peat mass loss (e.g. Hornibrook et al., 2000; Kuhry and Vitt, 1996). Fourier Transform Infrared spectroscopy (FTIR) of organic matter has been widely used to characterize organic matter such as humic and fulvic acids and bulk peat (e.g. Holmgren and Norden, 1988; Niemeyer et al., 1992) and provides information about the relative abundance of functional groups. This method is thus used to identify humification processes based on a change of organic matter quality, as more recalcitrant moieties such as aliphatic or aromatic substances accumulate (e.g. Beer et al., 2008; Kalbitz et al., 1999; Cocozza et al., 2003). As decomposition predominantly occurs in the acrotelm, more decomposed peat reaching the catotelm was reported to release less DOC than undecomposed peat (Biester et al., 2006; Kalbitz and Geyer, 2002). Thus, an inverse relation of the peat degree of decomposition and DOC concentrations may be expected, although it needs to be kept in mind that the DOC quality and thus degradability may also change. Isotope ratios have been quantified as well as

BGD
8, 10543–10576, 2011

an indicator of decomposition processes. Changing isotope signatures were assumed to result from isotope fractionation by microbial processes, because of preferential utilization of ^{12}C (e.g. Kalbitz and Geyer, 2002; Novak et al., 1999). This interpretation is in line with Hornibrook et al. (2000) finding that C/N and $\delta^{13}C$ values in peat soils correlated. As changing vegetation, microhabitat or climate also affect $\delta^{13}C$ values, their interpretation with respect to decomposition or paleoclimatic conditions needs caution (Pancost et al., 2003; Price et al., 1997; Novak et al., 2010; Skrzypek et al., 2007). Other than $\delta^{13}C$, also $\delta^{15}N$ has been applied to track nitrogen transformation during decomposition in organic soils (Kalbitz et al., 2000).

The aim of this study was thus to elucidate organic matter decomposition patterns in Patagonian ombrotrophic bogs using a set of complementary decomposition indices as outlined above and consider sea spray input as a nutrient source, climatic conditions, and ash deposition as controlling factors. We expected advanced decomposition (i) under drier conditions and (ii) with increasing sea spray input and assumed a partial preservation of past climatic signals in the catotelm decomposition record. To this end, we chose three pristine sites with different precipitation and sea spray input. All sites were influenced by past volcanic eruptions, which led to more or less abundant tephra depositions.

2 Materials and methods

2.1 Site description

The bogs (SkyI, SkyII, PBr2) are located in southern Patagonia near Punta Arenas (Chile) (Fig. 1) and have been partly described by Biester et al. (2003). They are situated between the Magellanic Moorlands with up to 10 000 mm yr^{-1} and the Pampa grassland with less than 500 mm yr^{-1} of precipitation. Mean annual temperature is about 6.5 °C (Schneider et al., 2003). The prevailing sea spray input was estimated by mean bromide concentrations in the solid peat, as bromide is a major constituent

BGD
8, 10543–10576, 2011

of sea spray and is better retained in the peat than chloride (Biester et al., 2006). Highest precipitation occurs at the SkyI site (~ 1500 mm yr^{-1}). The vegetation of the central raised part is dominated by *Sphagnum* mosses (e.g. *Sphagnum magellanicum*), shrubs (e.g. *Empetrum rubrum*) and cushion plants (e.g. *Astelia pumila*) and reaches a peat thickness of 3 m (Biester et al., 2003; Kilian et al., 2003). Precipitation at the SkyII site is less, about 1000 mm yr^{-1}, as measured in close vicinity (Schneider et al., 2003). Cushion plants are absent, dominating species are *Sphagnum magellanicum* and *Empetrum rubrum* and hummock-hollow micro-topography is pronounced. Peat thickness reaches > 4 m in the central part (Ina Reisen, personal communication). The third site, PBr2, receives the least precipitation of 650–800 mm yr^{-1} (Heusser et al., 2000). The vegetation is dominated by *Empetrum rubrum, Sphagnum magellanicum*, sedges and rushes. Mean peat thickness is about 6.50 m (Kilian et al., 2003). At the SkyI and PBr2 sites, tephra layers from eruptions of volcanoes located in the southern Andes had previously been described (Kilian et al., 2003). All bogs are underlain by acidic and base-poor materials (Kleinebecker et al., 2008).

2.2 Field sampling

Field sampling was conducted in March/April 2010 in hollows. The water level was determined using piezometers (PVC) of 4 cm diameter, fully slotted and 1 m in depth. Hydraulic conductivity (k_H) was obtained using piezometers (PVC) of similar design and a slotted segment of 20 cm in 1, 2 or 3 m depth. Values of k_H in the catotelm were determined in slug tests on several occasions using a temperature and air pressure compensated water pressure transducer over several days with a temporal resolution of 1 min (Levelogger Gold and Barologger, Solinst, Georgetown, Canada), following the Hvorslev method as described in Fetter (2001). This method has been successfully applied in peatland environments (e.g. Chason and Siegel, 1986; Fraser et al., 2001; Baird et al., 2008).

Peat samples were collected using a Russian peat corer (Eijkelkamp Agrisearch Equipment BV, Giesbeek, Netherlands). Cores were extracted to a depth of 300 cm in

BGD
8, 10543–10576, 2011

the SkyII and PBr2 bog and 180 cm in SkyI bog, divided into 10 cm segments and filled in plastic bags (Whirl Paks®, Nasco, Fort Atkinson, USA). Distinct volcanic ash layers were sampled separately and all samples stored at low temperatures before freeze drying and milling in the laboratory. Vegetation samples for isotope measurements and carbon and nitrogen contents were collected at the SkyI bog.

To extract greater volumes of pore-water samples for isotope measurements on DOM, we applied a pore-water suction sampler consisting of PE-sinter pieces (5 × 0.5 × 1 cm) inserted in a 3.50 m long rod at different depths and connected by tubing (2.5 × 4 mm, Polyurethane) to a stop-cock above the peatland surface. Suction samplers were installed at least one day prior to sampling and samples taken over a maximum period of two days by standard PE syringes, discarding the first milliliters of sampled water. The suction technique had a resolution of 20 cm to a max. depth of 195 cm and a 30 cm resolution beyond to max. 345 cm. Samples were transferred and stored in 125 ml PE-flasks (Nalgene).

2.3 Analytical procedures

For solid phase characterization, FTIR-spectra of the ground peat samples were obtained using a Vector 22 FTIR spectrometer (Bruker Optik, Ettlingen, Germany; absorption mode, subsequent baseline subtraction) on KBr pellets (200 mg dried KBr and 2 mg sample). Measurements were recorded from 4500 to 300 cm^{-1} using a resolution of 2 cm^{-1}. A number of 32 scans per sample were averaged. Absorption peaks indicative of structural units in organic matter were identified according to Senesi et al. (1989) and Niemeyer et al. (1992) and used as an indicator for peat organic matter quality (Fig. 3). Absorption bands at 950–1170 cm^{-1} (~ 1090 cm^{-1}) are allocated to OH vibrations of polysaccharides. Absorption at ~ 1420 cm^{-1} is ascribed to OH deformations and CO stretch of phenols or CH deformation of CH_2 or CH_3 groups (phenolic and aliphatic structures), at ~ 1510 cm^{-1} to aromatic C=C or to CO of amide groups. The ~ 1630 cm^{-1} region is indicative of aromatic C=C and asymmetric COO^-

BGD
8, 10543–10576, 2011

group vibrations (lignin and other aromatics and aromatic or aliphatic carboxylates) and $\sim 1720\,cm^{-1}$ of CO stretch of carbonyl and carboxyl groups (carboxylic acids and aromatic esters). To determine relative abundances of functional groups as a humification index, ratios between peak intensities for the following wavenumbers (given in cm^{-1}) with respect to polysaccharides ($1090\,cm^{-1}$) were calculated: 1720/1090; 1630/1090; 1510/1090 and 1420/1090 (Holmgren and Norden, 1988; Niemeyer et al., 1992).

As minerals may interfere with interpretation of FTIR-spectra of organic matter, ash rich samples were examined with X-ray Diffraction (XRD; Siemens D5000, Co K_α radiation; 2θ range 2° to 80°). Absorption bands of detected minerals in the FTIR-spectra were identified after Marel and Beutelspacher (1976). For identification of volcanic ash layers, metal concentrations of the peat samples (Rb, Sr, and Zr) were determined by an energy-dispersive miniprobe multielement analyzer (EMMA), which is a small desktop X-ray Fluorescence analyzer (XRF) system.

Dissolved organic carbon (DOC) concentrations were quantified in 0.45 µm filtered samples using a total carbon analyzer (Shimadzu TOC 5050). Pore-water samples with greater volume for DOC and dissolved organic nitrogen (DON) isotope analysis were filtered, frozen in an ethanol bath (−60 °C) in round bottom flasks and subsequently freeze-dried.

Ratios of $^{13}C/^{12}C$ and $^{15}N/^{14}N$ and total carbon and nitrogen were quantified in dried bulk plant material, peat and DOM on mass basis using an elemental analyzer (CE instruments NA 1108, Milano, Italy), connected via ConFlo III interface to a delta S IR-MS (Thermo Finnigan MAT, Bremen, Germany). Isotope signatures are given in the common δ-notation $\delta‰ = ((R_{sample}/R_{standard}) - 1) \times 10^3$, relative to the V-PDB-standard or N_2 in ambient air.

Statistical analyses were performed using PASW Statistics 18.0 (IBM Corporation). All data were tested for correlation with a level of significance (p) of 0.01 and 0.05 (Pearson, two-tailed).

BGD
8, 10543–10576, 2011

3 Results

3.1 Water table and hydraulic conductivity

The mean water table level over six weeks of the measurement period was 9 ± 3 cm at the PBr2 site, 12 ± 3 cm at the SkyI site, and 15 ± 2 cm at the SkyII site (Table 1). Head recovery in the slug tests was s-shaped. The hydraulic conductivities reached 10^{-6} m s^{-1} in 1 m depth and 10^{-8} m s^{-1} in 2 and 3 m depth. At the PBr2 site hydraulic conductivity in 2 m depth was 10^{-6} m s^{-1} and thus higher than at the other sites.

3.2 Ash deposits and sea spray input

Several tephra layers were identified by elemental concentrations of Rubidium, Strontium and Zirconium (Fig. 2). Ash layers in the PBr2 record at around 175 cm and in the SkyII record at around 265 cm could be related to the Mt. Burney eruption 4250 yr BP. In the SkyII record, two other layers in 125 cm and 200 cm depth were identified. Two small Rubidium peaks in 45 cm and 115 cm depth at the PBr2 record may also indicate ash layers. At the SkyI site, no tephra layers were evident from trace metal concentrations, except of two small peaks of Rubidium in 105 cm and Zirconium in 145 cm depth. At 180 cm depth, high metal concentrations indicated the influence of the underlying mineral rich sediment.

Following mean bromide concentrations in the solid peat, the SkyII bog received less sea spray (mean Br concentration of 48 mg kg^{-1} dry weight) than the other two bogs (SkyI: 86 mg Br kg^{-1}; PBr2: 97 mg Br kg^{-1}).

3.3 Spectroscopic characterization of organic matter and C/N ratio (peat quality)

Comparing XRD and FTIR-spectra, we found an interference mainly of feldspar in the ash layers and in the deepest peat sample of the SkyI site (FTIR-spectra see Fig. 3). Feldspar bands in FTIR-spectra are found at 400–800 nm^{-1} and in the Polysaccharide

BGD
8, 10543–10576, 2011

region, thus FTIR results in ash layers were not interpreted as humification index. All ratios (1720/1090, 1630/1090, 1510/1090 and 1420/1090) generally increased with depth, which meant a relative decrease of polysaccharides and a relative increase of aromatic, carboxylic, amid and phenolic moieties. As an example, the 1630/1090 ratio was correlated (Pearson) with depth with an r of 0.508 (PBr2) to 0.762 (SkyI) at the 0.01 level of significance (data not shown). Highest humification indices were observed at the PBr2 site. As the four FTIR-ratios given in Table 2 highly correlated with each other ($r > 0.83$, $p < 0.01$), only the 1630/1090 profile is shown in Fig. 4. Ratios of C/N of the solid phase inversely correlated with calculated FTIR-ratios at a 0.01 level of significance using all data ($N = 60$; see Table 2). Correlation coefficients ranged from −0.310 (PBr2, not significant) to −0.660 (SkyII, $p < 0.01$), reaching −0.777 (SkI, $p < 0.01$) using data of the individual sites only (not shown) and distinct deviations from the inverse relationship were obvious e.g. at the SkyII site below 125 cm and at the PBr2 site below 175 cm (Fig. 4). Compared to FTIR humification indices, C/N ratios were not correlated with depth, except of the record of SkyI.

In the PBr2 profile, humification was high, along with narrow C/N ratios (∼ 40) in the top 50 cm, while humification declined to 0.7–0.9 and C/N increased below to > 80. From 100 cm downward, this trend reversed and above the volcanic ash layer in 175 cm depth, the humification index peaked again (∼ 1.3) along with narrow C/N (50–55). In profiles of the SkyI and SkyII sites, the humification was similar in the upper meter and highest or high C/N occurred at the uppermost sample mostly consisting of fresh plant material. Beneath, in the SkyI record the index sharply increased and C/N decreased to a plateau. In the SkyII peat, humification was slightly lower than at the other sites, generally increasing with depth, but peaks seemed to be positioned near ash layers (Fig. 4). Ratios of C/N were mostly inversely related to humification down to a depth of 150 cm. Below, C/N ratios decreased only slightly with depth, in spite of consistently increasing humification.

BGD
8, 10543–10576, 2011

3.4 Dissolved organic carbon (DOC)

DOC concentrations ranged from $< 30\,mg\,l^{-1}$ to $160\,mg\,l^{-1}$, and mostly increased with depth (Fig. 4) as observed for the humification index in the solid peat (see correlations in Table 2). The three sites had similar concentrations in the upper 1 m (30–55 $mg\,l^{-1}$), but differed at greater depths. At the PBr2 site, concentrations were lowest, increased little with depth up to a concentration of $64\,mg\,l^{-1}$ and followed more the pattern of C/N. At the Sky sites, DOC concentrations followed the trend of the FTIR humification index. Concentrations of DOC at the SkyI site peaked at 160 cm near the peat base at $148\,mg\,l^{-1}$. The SkyII bog showed highest concentrations and the greatest gradient of all sites and peaked at 245 cm depth at $258\,mg\,l^{-1}$. This peak coincided with a volcanic ash layer and a high degree of humification. Below this ash layer DOC concentrations decreased again.

Values of C/N of the DOC were generally lower than in the solid phase (Fig. 4). Trends seemed to be related to the FTIR humification index of solid peat at all sites, but this could not be verified statistically (not shown).

3.5 Carbon and nitrogen isotope signatures

Carbon isotope signatures in the solid phase at all sites were around $\sim -26.5 \pm 1$ ‰ with exception of a lower value in the uppermost sample (fresh vegetation) of the SkyI site (Fig. 4). Values only weakly correlated with C/N (SkyI, leaving out the vegetation sample) or inversely with FTIR humification indices (SkyII and lumped data, PBr2 not significant) and correlations are thus not presented. From visual examination of the profiles, $\delta^{13}C$ values followed C/N ratios quite well, except of uppermost samples and few points near ash layers (PBr2, SkyII). At the SkyI site, $\delta^{13}C$ values increased to a maximum of −25.7 ‰ at 75 cm and decreased again below, following the C/N pattern. At the SkyII site, signatures on average decreased with depth and only partly followed the C/N pattern. In the PBr2 record, there was no trend in $\delta^{13}C$ values over depth but values were less negative compared to the other bogs and, interestingly, in phases

BGD
8, 10543–10576, 2011

of high decomposition the $\delta^{13}C$ pattern partly followed C/N ratios in a positive way (e.g. upper 75 cm and 125–150 cm). Isotope signatures of vegetation samples varied between −24.5 ‰ and −29.2 ‰ for carbon and between −11.2 ‰ to 1.2 ‰ for nitrogen (Table 3). The $\delta^{15}N$ signatures in the peat solid phase fluctuated between −3 ‰ and +3 ‰ over depth and could not be related to any decomposition index.

Values of $\delta^{13}C$ in the DOC fraction ranged from −28.1 ‰ to −24.4 ‰. Values at the PBr2 site were again less negative (∼ −26.7 ‰) compared to the other two bogs (SkyI ∼ −27.3 ‰ and SkyII ∼ −27.1 ‰). Highest ^{13}C content coincided with presence of an ash layer at 175 cm (PBr2) or 250 cm (SkyII), strongest ^{13}C depletion was observed in the upper profile at the Sky bogs. Values of $\delta^{13}C$ for DOC were similar or more negative than for the solid peat at the SkyI and the SkyII site. Contrarily, at the PBr2 site, $\delta^{13}C$ of DOC were either similar to or less negative compared to solid peat carbon.

Compared to DOC, DON was enriched in ^{15}N with depth by 2 ‰ to 15 ‰ compared to solid phase nitrogen. Values of $\delta^{15}N$ in DON were inversely correlated with solid phase $\delta^{15}N$ at the PBr2 site ($p < 0.05$), and positively correlated with the FTIR derived humification index for the lumped dataset and for the PBr2 site ($p < 0.01$ and $p < 0.05$, respectively).

4 Discussion

4.1 Peat decomposition

Taking the FTIR measurements as a qualitative parameter of decomposition of organic matter (Cocozza et al., 2003; Kalbitz et al., 1999), we could observe a generally increasing humification index with depth at all three sites. This pattern had previously been reported for northern temperate peatlands (Beer et al., 2008; Cocozza et al., 2003). As expected from previous studies, the C/N ratio as an indicator of peat mass loss during decomposition (Kuhry and Vitt, 1996) also showed a mostly consistent pattern, with lower C/N values with increasing humification. Indeed these two parameters were negatively correlated at our sites (C/N to 1630/1090; $r = 0.546$, see Table 2).

BGD
8, 10543–10576, 2011

However, in contrast to the FTIR-ratios, C/N ratios were not significantly correlated with depth, and deviations of the two decomposition parameters occurred as reported in the study of Borgmark and Schoning (2006). Ratios of C/N mainly ranged from 40 to 100, which is comparable to previously reported values for bog vegetation and peat (e.g. Hornibrook et al., 2000; Biester et al., 2003; Malmer and Holm, 1984). Lowest humification indices of the three investigated bogs occurred at the *Sphagnum* dominated SkyII bog with the greatest distance to the ocean and least sea spray input. In both Sky bogs a steep increase of humification (~ 0.5 to 0.8) and vice versa a decrease in C/N was detected in the upper oxic layer, where most decomposition processes take place before the organic matter is buried in the catotelm (Clymo, 1984). This was less obvious in the PBr2 profile, where high humification indices and low C/N ratios occurred in the upper 50 cm, suggesting increased decomposition and less peat accumulation in the last hundreds of years. Humification indices from FTIR measurements in the peat of the PBr2 site (0.7 to 1.4) exceeded values observed at the other sites, but were still lower compared to values reported by Beer et al. (2008) for the Canadian Mer Bleue Bog (1.00 to 1.73 from 50 to 330 cm depth)

Decomposition indices fluctuated with depth, probably reflecting environmental influence. As described by Clymo (1984) and Cocozza et al. (2003) decomposition is most intense in the acrotelm while there is little or no further change in the degree of decomposition in the catotelm. Changes in the humification index thus presumably represent changes in decomposition processes in the acrotelm and therefore changes in environmental conditions, i.e. different climate and resulting differences in decomposition and peat accumulation (Borgmark and Schoning, 2006; Kuhry and Vitt, 1996). This has also been investigated at one site in Patagonia to derive paleoclimatic conditions for the late-glacial and Holocene (McCulloch and Davies, 2001).

In the SkyI bog two different phases of decomposition occurred based on the humification index and C/N ratio. In the upper peat profile from 30–100 cm the humification index was low around 0.7 and C/N high, between 60 and 100. This suggests rapid peat growth under wet conditions (Borgmark and Schoning, 2006; Kuhry and Vitt, 1996).

BGD
8, 10543–10576, 2011

Below 100 cm peat decomposition was more advanced, which may indicated exposure of the material to drier conditions (Borgmark and Schoning, 2006). On the other hand the deeper peat may also have originated from a minerotrophic fen, as described in Kilian et al. (2003) for the center of the bog.

In contrast, in the PBr2 peat was more decomposed in the upper 75 cm and below 150 cm, i.e. C/N ratios were low and humification index high. A low C/N ratio in the vegetation suggested better nutrient supply and a more easily decomposable litter due to sea spray input, less precipitation, and different vegetation (Kleinebecker et al., 2007, 2008). Peat was also strongly decomposed near the ash layer at 175 cm. Between 75 and 150 cm depth peat had apparently accumulated more rapidly, as we infer from high C/N ratios and a low humification index. Biester et al. (2003) reported similar C/N ratios for the PBr2 site and found the same pattern of decomposition. This indicates a change in conditions in the past. High input of sea spray also occurred at the SkyI bog, but here this did not translate into higher decomposition, possibly because of the precipitation of around 1500 mm and sloped topography of the peatland.

In the SkyII bog the humification index increased with depth with some fluctuations but this trend was less visible in C/N ratios. Two ash layers apparently accelerated decomposition processes also here, as low C/N ratios and high humification indices occurred above the ash layers. Noticeable were two peaks of high C/N ratios and low humification, i.e. rapid peat growth at 50–75 cm and 140–150 cm depth, following the suggested interpretation of Kuhry and Yavitt (1996).

4.2 Decomposition and isotopic signatures of solid peat

Carbon isotope ratios in the solid phase varied only in a narrow range of 2 ‰ around −26.5 ‰, despite larger relative differences of decomposition degree with depth. Differences between the investigated sites were small. Values and variation of $\delta^{13}C$ fell into the range found in our vegetation and reported for *Sphagnum* and other vegetation (Hornibrook et al., 2000; Rice and Giles, 1996; Price et al., 1997; Kleinebecker et al., 2009). With few exceptions peat was generally depleted in ^{13}C with depth. As

BGD
8, 10543–10576, 2011

δ^{13}C values were mostly low in more decomposed peat and decomposition processes should result in δ^{13}C enrichment in the residual peat (Nadelhoffer and Fry, 1988; Novak et al., 1999), the δ^{13}C record was thus not the result of decomposition (see also Jones et al., 2010). It probably reflects other factors, such as changes in the vegetation (Hornibrook et al., 2000), moisture (Novak et al., 2010) or temperature (Jedrysek and Skrzypek, 2005; Skrzypek et al., 2007) during peat formation. Drier or warmer conditions, for example, lead to a more negative carbon isotope signature in mosses according to the latter studies. Following the studies of Borgmark and Schoning (2006) or Kuhry and Vitt (1996), drier conditions would result in faster decomposition, i.e. lower C/N ratios and high humification indices in the peat record. Particularly low C/N ratios and advanced humification were attributed to especially dry conditions and a secondary decomposition of previously buried peat (Borgmark and Schoning, 2006). Such phases may have occurred e.g. in the upper meter and below 150 cm at the PBr2 site, below 100 cm at the SkyI site and below 200 cm at the SkyII site. In these phases more negative δ^{13}C occurred when compared to other parts of the profiles.

To infer such climatic signals without reservations is difficult, though. Values of δ^{13}C in peat can be affected by plant uptake of recycled carbon from methane, an effect that is highly variable (Price et al., 1997; Raghoebarsing et al., 2005), but may especially occur under warmer conditions (Jones et al., 2010). In this regard, also the genesis of a bog may play a role. The PBr2 bog is located in a bowl-shaped depression that probably caused wet conditions; also under wet conditions, high CH_4 production can cause an uptake of light carbon from oxidized CH_4 (Jones et al., 2010), leading to the low δ^{13}C values below 200 cm depth. Low δ^{13}C values at the bottom part of the SkyI profile could also be due to the minerotrophic origin of the peatland, as low δ^{13}C in bulk peat were also observed in a minerotrophic site (Knorr et al., 2008) or in phases of minerotrophy (Jones et al., 2010). Paleoclimatic interpretation of the peat profiles is thus not straightforward. Individual factors such as climate, changes in moisture, nutrient input or vegetation, and peatland genesis may all influence the indices and confound the interpretation.

BGD
8, 10543–10576, 2011

Values of δ^{15}N in the solid phase ranged from −3‰ to +3‰, as also observed by Novak et al. (1999), but were neither related to decomposition degree nor to N contents. Greatest changes occurred in the upper 5–10 cm. Deeper into the peat δ^{15}N values were rather constant around 0‰, suggesting that atmospheric N was the primary N source (Jones et al., 2010). Data on N fixation activity and its contribution to total N inputs in peatlands are scarce (e.g. Kravchenko and Doroshenko, 2003) but the range of δ^{15}N in the vegetation samples was rather great compared to the range of δ^{15}N in peat. Our results for vegetation samples agree with previous measurements of Kleinebecker et al. (2009) for the same Patagonian region (Table 3). Thus, differences from litter input seemed to be leveled out. Only few δ^{15}N values have been reported so far for the investigated depths, though. Thus, the use of δ^{15}N measurements to trace decomposition in solid peat is so far not well constrained.

4.3 Volcanic ash layers and their impact on decomposition

Kilian et al. (2003) investigated ash layers at some southern Patagonian sites and also at the PBr2 and SkyI sites. The most prominent ash layer in these bogs originated from an eruption of Mt. Burney dated to 4254 ± 120 cal yr BP in Kilian et al. (2003) and 3830 ± 390 yr uncalib. ^{14}C age by Stern (2008). We identified this layer due to its thickness in 175 cm depth at the PBr2 and 265 cm in the SkyII record. All other volcanic eruptions, which could be recorded in our peat cores led to less ash deposition, were dispersed by root growth after deposition, and could not be easily distinguished. Therefore, we could use the Mt. Burney ash layer to compare peat accumulation. In the SkyI record, no ash layer could be identified for some reason.

Biester et al. (2003) reported peat accumulation rates for the PBr2 and SkyI bog (Table 4). The rates are in agreement with our interpretations because the accumulation rates at a site were low when we found more decomposed peat. The authors reported very low peat accumulation just above the Mt. Burney ash layer in their PBr2 profile (147–216 cm), where the peat was most strongly decomposed in this study. Phases of the higher accumulation rates coincided with phases of lower peat decomposition.

BGD
8, 10543–10576, 2011

Our SkyI depth profile was shorter, though, as the Mt. Burney eruption of 4250 yr BP occurred at 175 cm depth in the profile of Biester et al. (2003), but was not identified in our profile. The beginning of ombrotrophic peat formation at the PBr2 and SkyI sites was dated to 10 883 and 5952 yr BP (Table 4) (Kilian et al., 2003), our SkyI peat profile was thus younger. No accumulation rates are available for the SkyII bog, but comparing the depth of the 4250 yr BP tephra layer, it occurred at 265 cm depth, ~ 90 cm deeper than in the PBr2 bog. This indicates a greater overall accumulation of peat over the last 4000 yr, which is in accordance with the lower degree of decomposition in the SkyII bog. Using the Mt. Burney ash layer as a reference the SkyII bog on average accumulated about 0.06 cm yr^{-1} and the PBr2 bog 0.04 cm yr^{-1} from that time on.

The ash layers obviously had an influence on the degree of decomposition in the peat profiles. We want to point out that the very low values of the humification index within in the ash layer should not be taken in account, because of interferences of minerals in the FTIR-spectra (Marel and Beutelspacher, 1976). Especially above the Mt. Burney eruption around 4250 yr BP we observed a high humification index and medium to low C/N ratios in the PBr2 and SkyII record. Above the second prominent ash layer at 125 cm in the SkyII record, the C/N ratio and the humification index again peaked, albeit more weakly. Biester et al. (2003) suggested that low C/N values determined above tephra layers could be a result of increased decomposition due to the nutrient-rich ash deposition. This could result in enhanced microbial activity and organic matter mineralization. Hotes et al. (2010) reported an increase in pH, electric conductivity, sulfate and sodium concentrations, as well as nutrient release from decomposing plant material after volcanic ash deposition. After deposition, alkali loss is a typical phenomenon due to glass alteration of the tephra (Kilian et al., 2003 and references therein). An input of electron acceptors, such as sulfate, could further lead to alkalinity production under anaerobic conditions (Stumm and Morgan, 1996), resulting in higher pH and a faster decomposition.

On the other hand, McCulloch and Davies (2001) investigated a bog nearby the PBr2 site at Puerto del Hambre and interpreted phases of highly humified peat as a result

BGD
8, 10543–10576, 2011

of drier climatic conditions. Such a phase also occurred above the 4250 yr BP tephra layer, which could result from a shift of previously arid to again wetter conditions at that time (Markgraf, 1993). Climatic changes should have affected all three sites in a similar manner, and indeed decomposition indices and carbon stable isotope signatures support drier or warmer conditions and intense decomposition above the Mount Burney ash deposit at the SkyII and PBr2 sites. Also the bottom layers of SkyI could indicate drier conditions, minding possible influence of minerotrophic conditions on the indices. Although these interpretations may be plausible it seems unlikely that paleoclimatic variations are the sole explanation of the decomposition patterns because the three sites' records are not very similar. Following previous paleoclimatic interpretation of decomposition indices and $\delta^{13}C$ (Borgmark and Schoning, 2006; Jones et al., 2010; Skrzypek et al., 2007), the climate following the Mount Burney eruption was dry or warm, followed by a shift towards wetter conditions favoring peat growth (wider C/N ratios, lower humification), corroborating findings of Markgraf (1993). However, in our profile this trend ceases and is reversed at a depth of ~ 100 cm at the PBr2 site, again towards drier conditions and intense decomposition until present time. At the SkyII site, the trend towards wetter conditions (Markgraf, 1993) is interrupted by a second, undated ash deposit, followed by again higher decomposition. Thereafter, climatic conditions seemed again to become wetter or cooler. Such phases could, however, not be identified in the PBr2 record. Thus, climate induced signals at the sites may be masked by the influence of ash layers. Furthermore, diminished peat accumulation in the upper profile due to strong decomposition and drier conditions at the PBr2 site are not obvious at the other sites. They seem to reflect changes in rather local, site-specific factors. Following these interpretations, we propose that in bogs of this region of Patagonia the record of organic matter decomposition reflects a mixture of influences stemming from ash deposits, sea spray input, and paleoclimatic forcing. Using the – admittedly coarse – organic matter decomposition record to reconstruct climatic signals thus involves large uncertainty.

BGD
8, 10543–10576, 2011

4.4 Decomposition versus DOC concentrations and DOM isotopic signatures

In spite of differences in peat decomposition degree, DOC concentrations were very similar in the upper meter of all three sites. Deeper into the peat larger differences occurred. DOC concentrations observed at the PBr2 site agreed with reported DOC concentration ranges of 20 to 60 mg l^{-1} for northern peatlands (Blodau, 2002). At the Sky sites concentrations increased with depth by a factor of 3 (SkyI) and 5 (SkyII) and reached >250 mg l^{-1}. DOC concentrations >200 mg l^{-1} have rarely been reported (e.g. Clymo and Bryant, 2008).

A negative relation of DOM concentrations with the degree of peat decomposition has been reported (Kalbitz and Geyer, 2002; Biester et al., 2006). Generally, concentrations at the PBr2 site, with the highest humification index, were also low. Concentrations positively correlated with C/N ratios ($r = 0.712$, $p < 0.05$), as described in the study of Biester et al. (2006) before for this site. Highest DOC concentrations occurred at the SkyII site, with lowest humification index. In both Sky sites, however, concentrations correlated positively with the FTIR derived humification index (1630/1090 ratio, $r = 0.839$, $p < 0.01$ for the SkyII site; $r = 0.839$, $p < 0.05$ for the SkyI site), which is in conflict with the mentioned earlier work.

A redistribution of DOM could explain this discrepancy, but seems unlikely based on the low hydraulic conductivities and the low diffusion coefficient of DOM in the deeper peat (Beer et al., 2008; Biester et al., 2006; Cornel et al., 1986). Hydraulic conductivities ranged from 10^{-8} to 10^{-6} m s^{-1} and were similar as in a Canadian bog investigated by Fraser et al. (2001) but low compared to other peat bogs, where often 10^{-6} m s^{-1} to 10^{-5} m s^{-1} were found (Baird et al., 2008; Chason and Siegel, 1986). The factors that control DOC concentration are difficult to identify from our data. Elevated DOM concentrations occurred near ash layers and in the deeper peat potentially formed under minerotrophic or under drier climatic conditions at the Sky sites, but not at the PBr2 bog. Biester el al. (2006), further hypothesized that dry-falling may have occurred at the SkyI site, but not at the PBr2 site. The decomposition records, however, support

BGD
8, 10543–10576, 2011

also periodic drying at the PBr2 site. Such periodic dry falling of peatlands could have redistributed pore waters (Siegel et al., 1995) and thus obscure relations of DOC concentrations with solid phase properties. To identify the reasons for the differences in DOC concentrations with depth and between sites more research would be needed.

Kalbitz and Geyer (2002) related enhanced humification of DOM to an enrichment of ^{13}C in DOM. This could partly be confirmed by our data, as the $\delta^{13}C$ and the C/N ratio in the DOM were correlated ($p < 0.05$) at the PBr2 and SkyI sites but not at the SkyII site. Clymo and Bryant (2008) found DOM to be consistently enriched in ^{13}C compared to the solid peat. In our data, in the Sky bogs DOM was depleted in ^{13}C, but approached values of the solid phase with depth. In the more decomposed peat of the PBr2 bog, DOM became enriched in ^{13}C with depth compared to the solid phase. Thus, there was a relative enrichment of ^{13}C in DOM with depth, indicating preferential loss of ^{12}C during microbial modification. This was further supported by low C/N and increasing enrichment of ^{15}N in DOM. The latter indicates a repeated microbial recycling of N in DOM, which would be in line with a strong N deficiency at the sites. Enrichment of ^{15}N due to higher humification was described by Dijkstra et al. (2008), as N recirculation is leaky with respect to lighter isotopes. Interestingly, ^{15}N in DOM seemed to parallel trends of C/N in the solid peat, although this could not be verified statistically for the SkyII site, potentially indicating more intense N recycling in peat of higher C/N ratios. At this latter site, the profile of DOC concentrations and isotopic signatures seemed to be somehow displaced compared to the solid phase profile, obscuring this relation. In contrast, Kalbitz and Geyer (2002) found low $\delta^{15}N$ values in highly humified DOM, but this may be explained by a varying contribution of DON supply from either the solid phase or organic matter mineralization.

5 Conclusions

The study demonstrated both similarities and differences in peat decomposition records of the investigated peatlands. In comparison with bogs in the boreal region,

BGD
8, 10543–10576, 2011

the peat in three examined Patagonian bogs was less decomposed, indicating a slower decomposition process. The deep peat was most strongly decomposed at all sites as indicated by the FTIR humification index, but small variations over depth reflected frequent changes in controlling conditions over time. As the individual decomposition records of the sites differed in spite of their proximity, a paleoclimatic interpretation of the data seems to be constrained by local, site specific factors. One of these factors likely is the input of sea spray whose fertilizing effect may have been responsible for more advanced decomposition and less peat accumulation at the PBr2 and SkyI sites. Advanced decomposition within the depth profiles seemed to be related to ash deposits and possibly to drier conditions in the past. Not all drier periods that have been described were reflected in all profiles, though, and effects of ash deposits or also minerotrophy may have been more important for changes in decomposition indices and $\delta^{13}C$ of the peat. Relative enrichment of ^{13}C in DOM compared to the surrounding peat reflected a preferential loss of ^{12}C due to mineralization of DOM. Enrichment of ^{15}N in DOM and consistent trends with solid peat C/N ratios over depth suggested microbial recycling of N under N deficient conditions. DOM concentrations did not relate to decomposition indices in a consistent way.

Acknowledgements. This study was in part supported by a Deutsche Forschungsgemeinschaft (DFG) grants to H. Biester and C. Blodau, a travel grant of the Deutsche Gesellschaft für Limnologie (DGL) to K.H. Knorr. Stable isotope measurements were conducted at the BayCEER Laboratory of Isotope-Biogeochemistry, headed by Gerhard Gebauer. The assistance of Silke Hammer, Martina Rohr, Karin Söllner, Heidi Zier, Yvonne Hermanns and Ina Reisen is greatly acknowledged.

References

Aselmann, I. and Crutzen, P. J.: Global distribution of natural freshwater wetlands and rice-paddies, their net primary productivity, seasonality and possible methane emissions, J. Atmos. Chem., 8, 307–358, 1989.

BGD
8, 10543–10576, 2011

Baird, A. J., Eades, P. A., and Surridge, B. W. J.: The hydraulic structure of a raised bog and its implications for ecohydrological modelling of bog development, Ecohydrology, 1, 289–298, doi:10.1002/eco.33, 2008.
Beer, J. and Blodau, C.: Transport and thermodynamics constrain belowground carbon turnover in a northern peatland, Geochim. Cosmochim. Ac., 71, 2989–3002, doi:10.1016/j.gca.2007.03.010, 2007.
Beer, J., Lee, K., Whiticar, M., and Blodau, C.: Geochemical controls on anaerobic organic matter decomposition in a northern peatland, Limnol. Oceanogr., 53, 1393–1407, 2008.
Biester, H., Martinez-Cortizas, A., Birkenstock, S., and Kilian, R.: Effect of peat decomposition and mass loss on historic mercury records in peat bogs from Patagonia, Environ. Sci. Technol., 37, 32–39, doi:10.1021/es025657u, 2003.
Biester, H., Keppler, F., Putschew, A., Martinez-Cortizas, A., and Petri, M.: Halogen retention, organohalogens, and the role of organic matter decomposition on halogen enrichment in two Chilean peat bogs, Environ. Sci. Technol., 38, 1984–1991, doi:10.1021/es0348492, 2004.
Biester, H., Selimović, D., Hemmerich, S., and Petri, M.: Halogens in pore water of peat bogs – the role of peat decomposition and dissolved organic matter, Biogeosciences, 3, 53–64, doi:10.5194/bg-3-53-2006, 2006.
Blodau, C.: Carbon cycling in peatlands – a review of processes and controls, Environ. Rev., 10, 111–134, doi:0.1139/A02-004, 2002.
Borgmark, A. and Schoning, K.: A comparative study of peat proxies from two eastern central Swedish bogs and their relation to meteorological data, J. Quaternary Sci., 21, 109–114, doi:10.1002/jqs.959, 2006.
Bragazza, L., Siffi, C., Iacumin, P., and Gerdol, R.: Mass loss and nutrient release during litter decay in peatland: the role of microbial adaptability to litter chemistry, Soil Biol. Biochem., 39, 257–267, doi:10.1016/j.soilbio.2006.07.014, 2007.
Bridgham, S. D., Pastor, J., Updegraff, K., Malterer, T. J., Johnson, K., Harth, C., and Chen, J. Q.: Ecosystem control over temperature and energy flux in northern peatlands, Ecol. Appl., 9, 1345–1358, 1999.
Chason, D. B. and Siegel, D. I.: Hydraulic conductivity and related physical properties of peat, Lost River Peatland, northern Minnesota, Soil Sci., 142, 91–99, 1986.
Clymo, R. S.: The Limits to Peat Bog Growth, Philos. T. Roy. Soc. B., 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. Ac., 72,

BGD
8, 10543–10576, 2011

2048–2066, doi:10.1016/j.gca.2008.01.032, 2008.
Cocozza, C., D'Orazio, V., Miano, T. M., and Shotyk, W.: Characterization of solid and aqueous phases of a peat bog profile using molecular fluorescence spectroscopy, ESR and FT-IR, and comparison with physical properties, Org. Geochem., 34, 49–60, 2003.
Cornel, P. K., Summers, R. S., and Roberts, P. V.: Diffusion of humic-acid in dilute aqueous solution, J. Colloid Interf. Sci., 110, 149–164, 1986.
Damman, A. W. H.: Regulation of nitrogen removal and retention in *Sphagnum* bogs and other peatlands, Oikos, 51, 291–305, 1988.
Dijkstra, P., LaViolette, C. M., Coyle, J. S., Doucett, R. R., Schwartz, E., Hart, S. C., and Hungate, B. A.: ^{15}N enrichment as an integrator of the effects of C and N on microbial metabolism and ecosystem function, Ecol. Lett., 11, 389–397, doi:10.1111/j.1461-0248.2008.01154.x, 2008.
Fetter, C. W.: Applied Hydrogeology, 4. ed., Prentice Hall, Upper Saddle River, NJ, 598 pp., 2001.
Fraser, C. J. D., Roulet, N. T., and Lafleur, M.: Groundwater flow patterns in a large peatland, J. Hydrol., 246, 142–154, 2001.
Freeman, C., Ostle, N., and Kang, H.: An enzymic "latch" on a global carbon store – a shortage of oxygen locks up carbon in peatlands by restraining a single enzyme, Nature, 409, 149–149, 2001.
Frolking, S., Roulet, N. T., Moore, T. R., Richard, P. J. H., Lavoie, M., and Muller, S. D.: Modeling northern peatland decomposition and peat accumulation, Ecosystems, 4, 479–498, 2001.
Godoy, R., Paulino, L., Oyarzún, C., and Boeckx, P.: Atmospheric N deposition in central and southern Chile: an overview, Gayana Bot., 60, 47–53, 2003.
Heusser, C. J., Heusser, L. E., Lowell, T. V., Moreira, A., and Moreira, S.: Deglacial palaeoclimate at Puerto del Hambre, subantarctic Patagonia, Chile, J. Quaternary. Sci., 15, 101–114, 2000.
Hogg, E. H.: Decay potential of hummock and hollow *Sphagnum* peats at different depths in a Swedish raised bog, Oikos, 66, 269–278, 1993.
Holmgren, A. and Norden, B.: Characterization of peat samples by diffuse reflectance FT-IR spectroscopy, Appl. Spectrosc., 42, 255–262, 1988.
Hornibrook, E. R. C., Longstaffe, F. J., Fyfe, W. S., and Bloom, Y.: Carbon-isotope ratios and carbon, nitrogen and sulfur abundances in flora and soil organic matter from a temperate-zone bog and marsh, Geochem. J., 34, 237–245, 2000.

BGD
8, 10543–10576, 2011

Hotes, S., Grootjans, A. P., Takahashi, H., Ekschmitt, K., and Poschlod, P.: Resilience and alternative equilibria in a mire plant community after experimental disturbance by volcanic ash, Oikos, 119, 952–963, doi:10.1111/j.1600-0706.2009.18094.x, 2010.

IFM GEOMAR, Leibniz-Institut für Meereswissenschaften an der Universität Kiel, SFB 574: https://sfb574.ifm-geomar.de/gmt-maps/, last access: 26 February 2011.

Jedrysek, M. O. and Skrzypek, G.: Hydrogen, carbon and sulphur isotope ratios in peat: the role of diagenessis and water regimes in reconstruction of past climates, Environ. Chem. Lett., 2, 179–183, doi:10.1007/s10311-004-0093-4, 2005.

Jones, M. C., Peteet, D. M., and Sambrotto, R.: Late-glacial and Holocene δ^{15}N and δ^{13}C variation from a Kenai Peninsula, Alaska peatland, Palaeogeogr. Palaeocl., 293, 132–143, 2010.

Kalbitz, K. and Geyer, S.: Different effects of peat degradation on dissolved organic carbon and nitrogen, Org. Geochem., 33, 319–326, 2002.

Kalbitz, K., Geyer, W., and Geyer, S.: Spectroscopic properties of dissolved humic substances – a reflection of land use history in a fen area, Biogeochemistry, 47, 219–238, 1999.

Kalbitz, K., Geyer, S., and Gehre, M.: Land use impacts on the isotopic signature (^{13}C, ^{14}C, ^{15}N) of water-soluble fulvic acids in a German fen area, Soil Sci., 165, 728–736, 2000.

Kilian, R., Hohner, M., Biester, H., Wallrabe-Adams, H. J., and Stern, C. R.: Holocene peat and lake sediment tephra record from the southernmost Chilean Andes (53–55° S), Rev. Geol. Chile, 30, 23–37, 2003.

Kleinebecker, T., Holzel, N., and Vogel, A.: Gradients of continentality and moisture in South Patagonian ombrotrophic peatland vegetation, Folia Geobot., 42, 363–382, 2007.

Kleinebecker, T., Holzel, N., and Vogel, A.: South Patagonian ombrotrophic bog vegetation reflects biogeochemical gradients at the landscape level, J. Veg. Sci., 19, 151–160, doi:10.3170/2008-8-18370, 2008.

Kleinebecker, T., Schmidt, S. R., Fritz, C., Smolders, A. J. P., and Hölzel, N.: Prediction of δ^{13}C and δ^{15}N in plant tissues with near-infrared reflectance spectroscopy, New Phytol., 184, 732–739, doi:10.1111/j.1469-8137.2009.02995.x, 2009.

Knorr, K.-H., Glaser, B., and Blodau, C.: Fluxes and ^{13}C isotopic composition of dissolved carbon and pathways of methanogenesis in a fen soil exposed to experimental drought, Biogeosciences, 5, 1457–1473, doi:10.5194/bg-5-1457-2008, 2008.

Kravchenko, I. K. and Doroshenko, E. V.: Nitrogen-fixing activity in peat soils from a raised bog, Microbiology, 72, 98–102, 2003.

BGD
8, 10543–10576, 2011

Kuhry, P. and Vitt, D. H.: Fossil carbon/nitrogen ratios as a measure of peat decomposition, Ecology, 77, 271–275, 1996.
Laiho, R.: Decomposition in peatlands: Reconciling seemingly contrasting results on the impacts of lowered water levels, Soil Biol. Biochem., 38, 2011–2024, doi:10.1016/j.soilbio.2006.02.017, 2006.
Malmer, N. and Holm, E.: Variation in the C/N-quotient of peat in relation to decomposition rate and age determination with ^{210}Pb, Oikos, 43, 171–182, 1984.
Marel, H. W. v. d. and Beutelspacher, H.: Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures, Elsevier Scientific Publishing Company, Amsterdam, 396 pp., 1976.
Markgraf, V.: Paleoenvironments and paleoclimates in Tierra del Fuego and southernmost Patagonia, South America, Paleogeogr. Paleocl., 102, 53–68, 1993.
McCulloch, R. D. and Davies, S. J.: Late-glacial and Holocene palaeoenvironmental change in the central Strait of Magellan, southern Patagonia, Paleogeogr. Paleocl., 173, 143–173, 2001.
Nadelhoffer, K. F. and Fry, B.: Controls on natural ^{15}N and ^{13}C abundances in forest soil organic matter, Soil Sci. Soc. Am. J., 52, 1633–1640, 1988.
Niemeyer, J., Chen, Y., and Bollag, J. M.: Characterization of humic acids, composts, and peat by diffuse reflectance Fourier-transform infrared-spectroscopy, Soil Sci. Soc. Am. J., 56, 135–140, 1992.
Novak, M., Buzek, F., and Adamova, M.: Vertical trends in δ^{13}C, δ^{15}N and δ^{34}S ratios in bulk Sphagnum peat, Soil Biol. Biochem., 31, 1343–1346, 1999.
Novak, M., Zemanova, L., Buzek, F., Jackova, I., Adamova, M., Komarek, A., Vile, M. A., Kelman Wieder, R., and Stepanova, M.: The effect of a reciprocal peat transplant between two contrasting Central European sites on C cycling and C isotope ratios, Biogeosciences, 7, 921–932, doi:10.5194/bg-7-921-2010, 2010.
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.
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.
Raghoebarsing, A. A., Smolders, A. J. P., Schmid, M. C., Rijpstra, W. I. C., Wolters-Arts, M., Derksen, J., Jetten, M. S. M., Schouten, S., Damste, J. S. S., Lamers, L. P. M.,

BGD
8, 10543–10576, 2011

Roelofs, J. G. M., den Camp, H., and Strous, M.: Methanotrophic symbionts provide carbon for photosynthesis in peat bogs, Nature, 436, 1153–1156, doi:10.1038/nature03802, 2005.
Rice, S. K. and Giles, L.: The influence of water content and leaf anatomy on carbon isotope discrimination and photosynthesis in Sphagnum, Plant Cell Environ., 19, 118–124, 1996.
Schneider, C., Glaser, M., Kilian, R., Santana, A., Butorovic, N., and Casassa, G.: Weather observations across the Southern Andes at 53° S, Phys. Geogr., 24, 97–119, 2003.
Segers, R. and Kengen, S. W. M.: Methane production as a function of anaerobic carbon mineralization: A process model, Soil Biol. Biochem., 30, 1107–1117, 1998.
Senesi, N., Miano, T. M., Provenzano, M. R., and Brunetti, G.: Spectroscopic and compositional comparative characterization of IHSS reference and standard fulvic and humic acids of various origin, Sci. Total Environ., 81-2, 143–156, 1989.
Siegel, D. I., Reeve, A. S., Glaser, P. H., and Romanowicz, E. A.: Climate-driven flushing of pore water in peatlands, Nature, 374, 531–533, 1995.
Skrzypek, G., Kaluzny, A., Wojtun, B., and Jedrysek, M. O.: The carbon stable isotopic composition of mosses: a record of temperature variation, Org. Geochem., 38, 1770–1781, doi:10.1016/j.orggeochem.2007.05.002, 2007.
Stern, C. R.: Holocene tephrochronology record of large explosive eruptions in the southernmost Patagonian Andes, B. Volcanol., 70, 435–454, doi:10.1007/s00445-007-0148-z, 2008.
Stumm, W. and Morgan, J. J.: Aquatic chemistry – chemical equilibria and rates in natural waters, in: Environmental Science and Technology, edited by: Schnoor, J. L. and Zehnder, A., Wiley-Interscience, New York, 1021 pp., 1996.
Yu, Z., Loisel, J., Brosseau, D. P., Beilmann, D. W., and Hunt, S. J.: Global peatland dynamics since the Last Glacial Maximum, Geophys. Res. Lett., 37, doi:10.1029/2010GL043584, 2010.

BGD
8, 10543–10576, 2011

Table 1. Mean water table and hydraulic conductivity in 1, 2 and 3 m depth at the three sites.

Site	Mean water level (cm below surface)	K_H ($m\,s^{-1}$) 1 m	K_H ($m\,s^{-1}$) 2 m*	K_H ($m\,s^{-1}$) 3 m*
PBr2	9 ± 3	3.5×10^{-6}	1×10^{-6}	3×10^{-8}
SkyI	12 ± 3	1.5×10^{-6}	1.5×10^{-8}	1.5×10^{-8}
SkyII	15 ± 2	2.5×10^{-6}	3.5×10^{-8}	1×10^{-8}

* In SkyI 2 m and 3 m Piezometer tubes were installed at the final depth of 1.80 m

BGD
8, 10543–10576, 2011

Table 2. Correlation coefficients after Pearson (r), with N as number of sample. Asterisks indicate different levels of significance. Only significant correlations are shown.

		FTIR 1720/1090	FTIR 1630/1090	FTIR 1510/1090	FTIR 1420/1090
FTIR 1720/1090	r	–			
	N				
FTIR 1630/1090	r	0.937[b]	–		
	N	77			
FTIR 1510/1090	r	0.834[b]	0.933[b]	–	
	N	77	77		
FTIR 1420/1090	r	0.921[b]	0.972[b]	0.974[b]	–
	N	77	77	77	
DOC (mg l^{-1})	r			0.505[b]	0.452[a]
	N			29	29
Peat N (%)	r	0.571[b]	0.625[b]	0.549[b]	0.540[b]
	N	60	60	60	60
Peat C (%)	r	0.715[b]	0.655[b]	0.566[b]	0.653[b]
	N	60	60	60	60
δ^{13}C (‰)	r	−0.311[a]	−0.303[a]	−0.357[b]	−0.325[a]
	N	60	60	60	60
Peat C/N	r	−0.446[b]	−0.546[b]	−0.490[b]	−0.469[b]
	N	60	60	60	60

[a] Correlation is significant on a level of 0.05 (2-tailed).
[b] Correlation is significant on a level of 0.01 (2-tailed).

BGD
8, 10543–10576, 2011

Table 3. Carbon and nitrogen isotope signatures and C/N of different plants of the SkyI site in comparison to values evaluated by Kleinebecker et al. (2009) at bogs in southern Patagonia.

Species	δ^{13}C (‰)	δ^{15}N (‰)	C/N
Astelia pumila	$-26.5^{a}/-26.0^{b}$	$-5.4^{a}/-5.6^{b}$	$74^{a}/43^{b}$
Empetrum rubrum	$-28.7^{a}/-28.2^{b}$	$-11.2^{a}/-9.7^{b}$	$104^{a}/71^{b}$
Marsippospermum grandiflorum	$-24.5^{a}/-25.3^{b}$	$1.2^{a}/2.3^{b}$	$36^{a}/46^{b}$
Nothofagus betuloides	-29.2^{a}	-3.4^{a}	77^{a}
Sphagnum magellanicum	$-29.1^{a}/-27.0^{b}$	$-1.0^{a}/-4.7^{b}$	$134^{a}/89^{b}$
Tetronicum magellanicum	-27.2^{a}	0.8^{a}	83^{a}

[a] this study
[b] mean values from Kleinebecker et al. (2009); C/N was calculated by mean total carbon and nitrogen content

BGD
8, 10543–10576, 2011

Table 4. Peat accumulation rates for the PBr2 and SkyI bogs from Biester et al. (2003) and peat ages from Kilian et al. (2003) since the beginning of ombrotrophic peat growth.

PBr2				SkyI			
Depth (cm)	Peat accum. (cm yr^{-1})	Peat age (cal yr BP) Depth (cm)	Age	Depth (cm)	Peat accum. (cm yr^{-1})	Peat age (cal yr BP) Depth (cm)	Age
0–63	0.057			0–68	0.062	68	858
63–147	0.133	70	855	68–120	0.069	120	1846
147–216	0.025	148	1481	120–244	0.026	244	5952
216–480	0.036	480	10 883				

BGD
8, 10543–10576, 2011

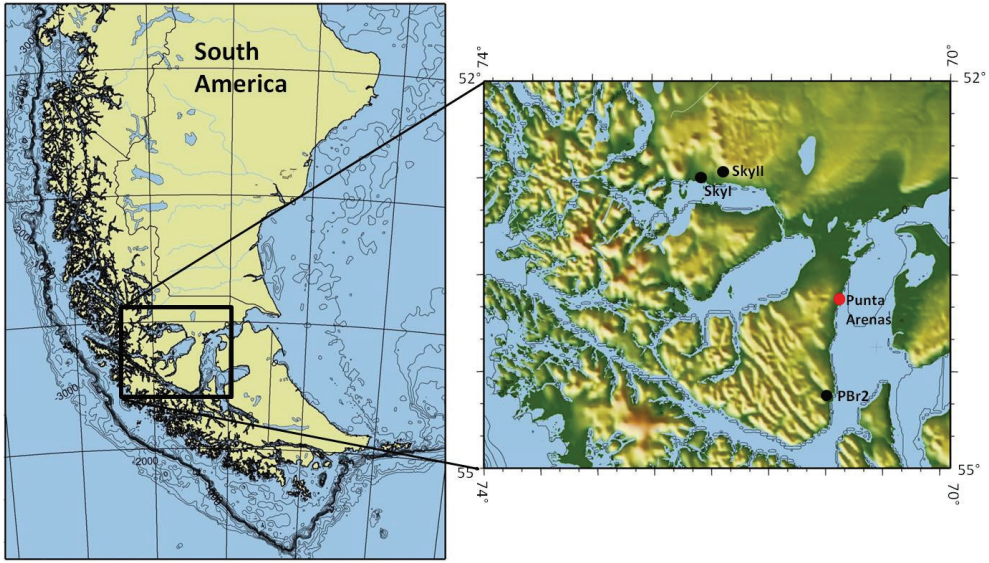

Fig. 1. Map of the study area in southern South America. Locations of the sampling sites are marked in the detailed map. Maps were generated online at https://sfb574.ifm-geomar.de/gmt-maps at 26 February 2011 (IFM-GEOMAR).

BGD
8, 10543–10576, 2011

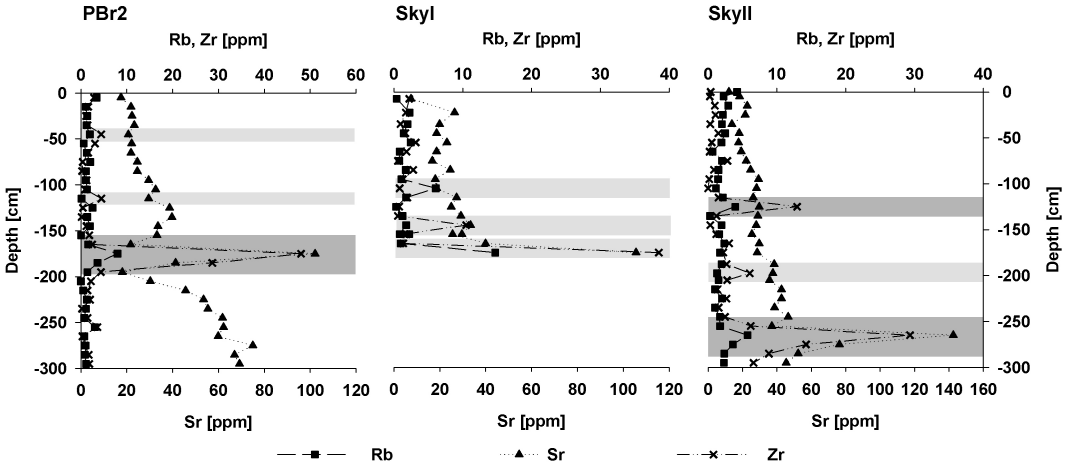

Fig. 2. Concentrations of Rubidium (solid squares), Strontium (solid triangles) and Zirconium (crosses) in the peat samples in parts per million. Clearly identified volcanic tephra layers are highlighted in gray. Less well defined tephra layers and underlying sediment in the SkyI record are highlighted by a lighter gray. The thick gray bands in the PBr2 and SkyII records indicate the deposit of the Mt. Burney eruption 4250 yr BP.

BGD
8, 10543–10576, 2011

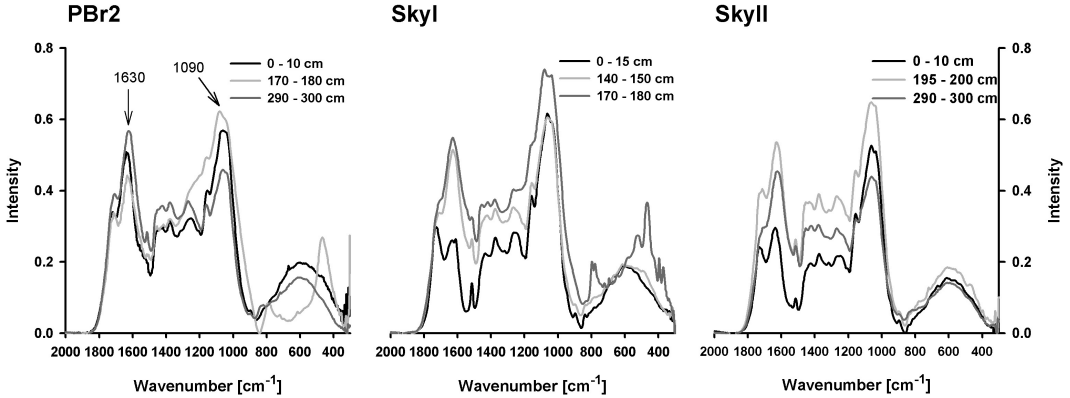

Fig. 3. FTIR-spectra of peat samples from the three bogs in different depths. Chosen samples represent upper, less decomposed peat (0–10 cm), deeper, highly decomposed peat and samples influenced by ash layer or underlying sediment (Pbr2 170–180 cm and Skyl 170–180 cm).

BGD
8, 10543–10576, 2011

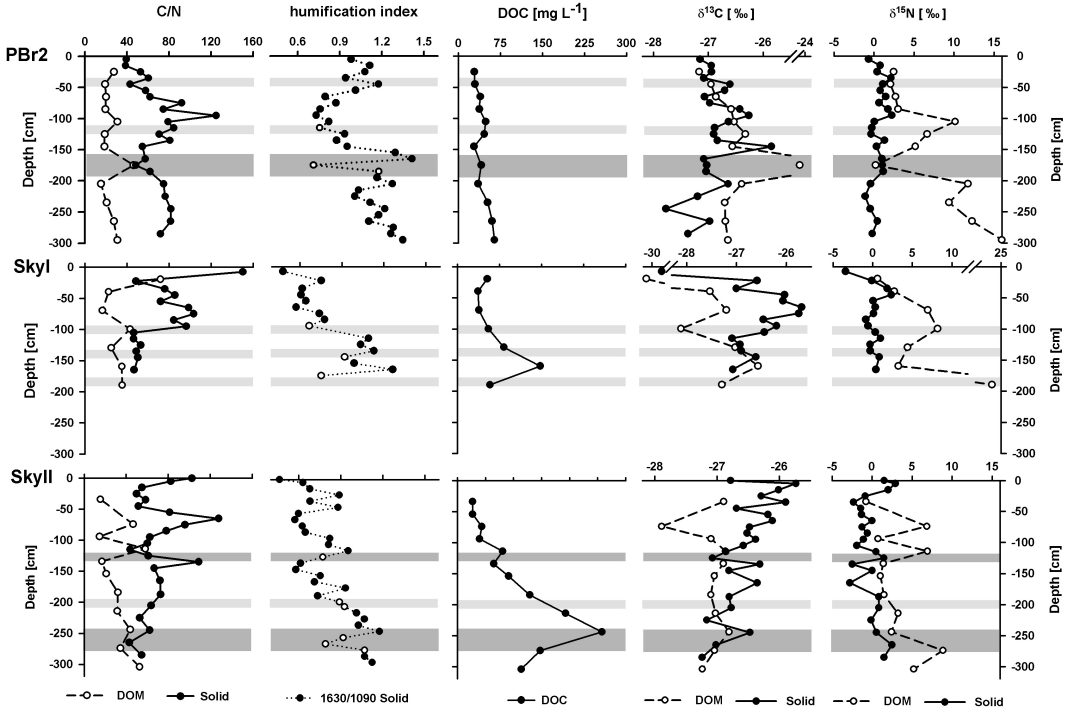

Fig. 4. C/N ratios of solid peat and DOM, FTIR derived humification indices (ratios of absorption at wavenumbers 1630/1090), DOC concentrations, $\delta^{13}C$ and $\delta^{15}N$ of solid peat and DOM at the sites PBr2 (top), SkyI (middle), and SkyII (bottom). Grey bands denote ash layers. Open symbols in profiles of humification indices indicate samples possibly influenced by ash deposits and need to be interpreted with caution. Note different scaling of isotope ratios.

BGD
8, 10543–10576, 2011