


Elemental and isotopic carbon and nitrogen records of organic matter accumulation in a Holocene permafrost peat sequence in the East European Russian Arctic



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ABSTRACT: A peat deposit from the East European Russian Arctic, spanning nearly 10 000 years, was investigated to study soil organic matter degradation using analyses of bulk elemental and stable isotopic compositions and plant macrofossil remains. The peat accumulated initially in a wet fen that was transformed into a peat plateau bog following aggradation of permafrost in the late Holocene (~2500 cal a BP). Total organic carbon and total nitrogen (N) concentrations are higher in the fen peat than in the moss-dominated bog peat layers. Layers in the sequence that have lower concentrations of total hydrogen (H) are associated with degraded vascular plant residues. C/N and H/C atomic ratios indicate better preservation of organic matter in peat material dominated by bryophytes as opposed to vascular plants. The presence of permafrost in the peat plateau stage and water-saturated conditions at the bottom of the fen stage appear to lead to better preservation of organic plant material. $\delta^{15}\text{N}$ values suggest N isotopic fractionation was driven primarily by microbial decomposition whereas differences in $\delta^{13}\text{C}$ values appear to reflect mainly changes in plant assemblages. Positive shifts in both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values coincide with a local change to drier conditions as a result of the onset of permafrost and frost heave of the peat surface. This pattern suggests that permafrost aggradation not only resulted in changes in vegetation but also aerated the underlying fen peat, which enhanced microbial denitrification, causing the observed ^{15}N -enrichment. Copyright © 2012 John Wiley & Sons, Ltd.

KEYWORDS: Arctic peatlands; permafrost; stable isotopes; elemental analyses; macrofossil analyses.

Introduction

Large amounts of carbon (C) and nitrogen (N) are stored in northern peatlands (Limpens *et al.*, 2006; Tarnocai *et al.*, 2009), and soil organic matter (SOM) in peat deposits plays a significant role in the global biogeochemical cycles of these important elements. Destabilization of the enormous stocks of peat SOM can potentially lead to accelerated emissions of greenhouse gases to the atmosphere (Davidson and Janssens, 2006). A positive feedback to climate change may result from degradation of peatland SOM as a consequence of warming at high latitudes, which are the regions most sensitive to climate change (Lemke *et al.*, 2007). Mechanisms that control degradation and stabilization of organic matter have been widely studied in recent years (Kracht and Gleixner, 2000; Davidson and Janssens, 2006), but much remains to be done to better understand these processes under different eco-climatic scenarios.

Stable isotope analysis of peat and other geological materials is an important tool for gaining insight into biogeochemical processes involved in SOM degradation and preservation (Balesdent *et al.*, 1987; Nadelhoffer *et al.*, 1996; Kracht and Gleixner, 2000) and also in paleoclimate studies (Jones *et al.*, 2010; Kaislahti Tillman *et al.*, 2010). However, interpretation of such records is not straightforward because many factors affect and control stable isotope variations. In addition, a large variety of vascular plants, mosses, algae, fungi, microorganisms and sedimentation processes influence the C and N isotope compositions of SOM.

Peat deposits are archives of ecosystem development, plant succession and past regional climate (Barber, 1993). Organic matter accumulated in these systems contains elemental and isotopic records that potentially can be used to reconstruct past

environmental conditions and cycling of C and N. Traditional methods and techniques in the study of past vegetation assemblages and degradation of peat include the analyses of plant macrofossil residues and peat humification (Chambers *et al.*, 2012). A disadvantage of the macrofossil method is the difficulty in properly identifying highly decomposed plant remains. The peat humification technique based on the alkaline extraction of humic matter imposes uncertainties on the interpretation of the measured signal, which is usually considered an indicator of decay; however, some results suggest that it may instead be a measure of initial botanical chemical compositions (Caseldine *et al.*, 2000). These potential limitations of traditional methods and techniques point towards the necessity of using alternative, complementary proxies for paleoenvironmental studies based on peat sequences.

To evaluate the effects of Holocene environmental changes on organic matter preservation and to investigate evidence of past C and N cycling in a peat sequence, we measured the concentrations of carbon, nitrogen and hydrogen (H), the atomic H/C and C/N ratios, and the stable C and N isotope compositions of organic matter in a peat core from the European Russian Arctic. These parameters are influenced by the biochemical plant compositions, peat diagenesis, and local and regional environmental events that drove changes in vegetation assemblages. We also incorporated plant macrofossil analyses in the study to complement and facilitate interpretation of the organic geochemical data.

Interpretive foundations for the organic matter elemental and isotopic compositions

Elemental compositions and atomic C/N and H/C ratios

Elemental ratios derived from organic matter C, N and H concentrations can provide information about the sources and

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preservation of this material. Atomic C/N ratios between 20 and 50 are typical of the vascular and mossy plants that are important to peat accumulations (e.g. Meyers, 1994). These relatively high C/N ratios commonly exist in shallow layers of recently deposited peat that has not undergone significant decomposition. In non-permafrost peatlands, C/N ratios decrease markedly in deeper peat layers as a result of progressive decomposition that removes more carbon than nitrogen (Kuhry and Vitt, 1996). In contrast, high C/N ratios are largely preserved in permafrost peatlands because perennially frozen conditions inhibit decomposition of organic matter (Vardy *et al.*, 2000).

Atomic H/C ratios in a peat profile can also provide clues to the chemical constitution and quality of the peat. Algal, herbaceous, woody and coaly sedimentary organic matter contain different proportions of hydrogen (Talbot and Livingstone, 1989). Algal organic matter tends to have more hydrogen-rich aliphatic components, whereas herbaceous and woody materials have increasingly more hydrogen-depleted aromatic components. Carbonaceous residues in coaly material have very low H contents (Talbot and Livingstone, 1989). These characteristics are reflected in atomic H/C ratios that also provide insight into the preservation of peat material (e.g. Ortiz *et al.*, 2004). Saturated H-rich organic compounds are characterized by high H/C ratios and tend to be readily consumed by bacteria. Algal material is consequently rapidly removed relative to herbaceous and woody materials. In addition, hydrogen-rich cellulose is more readily degraded than lignin-derived aromatic compounds, which tend to be more resistant to humification processes (Benner *et al.*, 1987; Kracht and Gleixner, 2000).

$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values

The $\delta^{13}\text{C}$ value of organic matter is a sensitive paleoenvironmental indicator that can provide information about ancient biogeochemical processes (Hayes, 1993) and has been investigated in permafrost and non-permafrost peats (Ortiz *et al.*, 2004; Alewell *et al.*, 2011). Plant $\delta^{13}\text{C}$ values are principally determined by photosynthetic processes (Farquhar *et al.*, 1989), but external factors can also affect $^{13}\text{C}/^{12}\text{C}$ ratios. Ménot and Burns (2001) determined that atmospheric CO_2 concentration, growth temperature and water stress influence $\delta^{13}\text{C}$ values of vascular plants and mosses in ombrotrophic bogs. Additional ^{13}C fractionation can result from interactions between roots, microorganisms and soil organic matter (Werth and Kuzyakov, 2010). Analysis of different tissues has identified

heterogeneity in $\delta^{13}\text{C}$ values in a single plant (Balesdent *et al.*, 1987), including branches and stems in *Sphagnum* (Loader *et al.*, 2007; Moschen *et al.*, 2009).

Degradation of organic matter may produce ^{13}C -enrichment in residual material because bacteria preferentially metabolize the ^{12}C -rich fraction (Skrzypek *et al.*, 2007). An increase in $\delta^{13}\text{C}$ values with depth and age in organic matter has been reported in different soils (e.g. Balesdent and Mariotti, 1998; Bol *et al.*, 1999). However, other studies have reported that during decomposition of vascular plant debris, selective assimilation of polysaccharides by bacteria produces a lignin-rich residue, resulting in more negative $\delta^{13}\text{C}$ values because lignins are ^{13}C -depleted relative to cellulose (e.g. Benner *et al.*, 1987). On the other hand, the isotopic source information of organic matter can be preserved in sediments for millions of years (Meyers, 1994). Skrzypek *et al.* (2010) also demonstrated that $\delta^{13}\text{C}$ values of peat remain well preserved and mainly reflect the C isotope composition of original peat-forming plant debris rather than post-depositional decay processes.

The stable isotope composition of nitrogen in wetland vegetation and peat has been less studied than carbon, and few data sets are available for comparison. Nadelhoffer (1996) reported that N mineralization of tundra plants and soil resulted in N isotope fractionation, causing more positive $\delta^{15}\text{N}$ values with depth and age of organic matter. During degradation, microorganisms appear to preferentially utilize ^{14}N , leaving soil organic matter ^{15}N -enriched, although nitrogen uptake by plants also may contribute to partitioning of ^{15}N and ^{14}N (Nadelhoffer *et al.*, 1996).

Study area, materials and methods

Lek-Vorkuta peat plateau

The peat profile was collected from a peat plateau in Lek-Vorkuta, Russia (Fig. 1). The region is located in the lowland tundra of North-east European Russia ($67^{\circ}25'\text{N}$, $63^{\circ}22'\text{E}$) ca. 35 km south-west of the city of Vorkuta in an area characterized by discontinuous permafrost. Modern vegetation covering the dry elevated flat surface of the peat plateau is dominated by dwarf shrubs such as *Vaccinium vitis-idaea* (lingonberry) and *Ledum palustre* (wild rosemary) and by lichens.

Peat collection

The LVPS4 peat section was collected in August 1999 by cutting slices from the upper 100 cm of the peat sequence

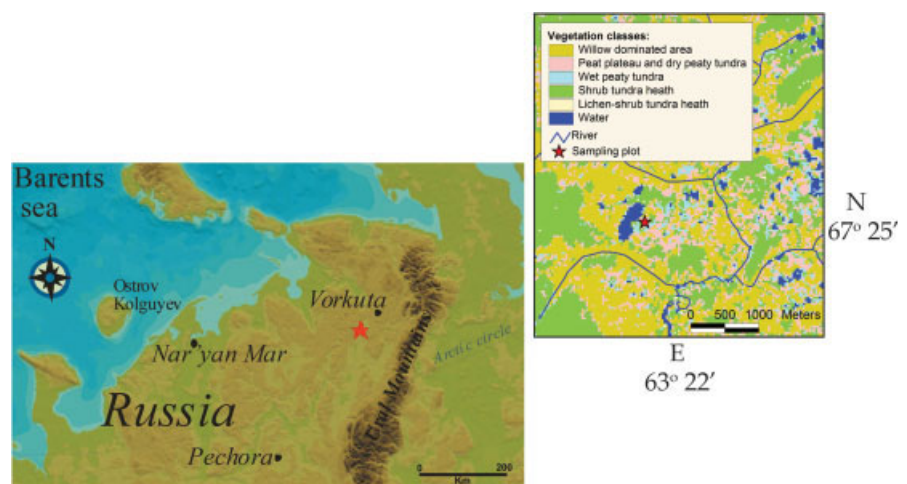


Figure 1. Map showing the study site in Lek-Vorkuta taken from Andersson *et al.* (2011), with land vegetation cover taken from Virtanen *et al.* (2004). This figure is available in colour online at wileyonlinelibrary.com/journal/jqs.

exposed next to a thermokarst lake. Core LVPS5B (100–240 cm) was collected in July 2000 ca. 40 m to the south-west of section LVPS4 by hammering a steel pipe into the frozen peat and extracting subsamples at ca. 10-cm intervals. Neither plant macrofossil nor geochemical records show abrupt transitions between the two profiles at the 100-cm level. The composite profile is consequently considered a continuous sequence that is hereafter referred to as core LVPS4 + 5B.

Plant macrofossil and radiocarbon analyses

Botanical remains in 12 peat samples were analyzed as described by Andersson *et al.* (2011). Four of those macrofossil samples were radiocarbon-dated. Plant macrofossil analysis of peat from 220 cm depth was performed because of geochemical changes observed at that horizon.

Elemental and isotopic analyses

Frozen peat samples were freeze-dried and then ground using a ball mill (Retsch GmbH type MM2). Two to three mg of each sample was used for elemental analysis (Carlo Erba NC2500). Total carbon (C), hydrogen (H) and nitrogen (N) contents were measured simultaneously at 1000 °C with respective standard deviations of 0.153, 0.117 and 0.089% (reproducibility). Five samples along the core were analyzed in duplicate. The second analysis included sample treatment with acid to remove any carbonate carbon. The two results showed no difference, and therefore we considered the total carbon content to be equivalent to the total organic carbon (TOC) in all samples. For carbon and nitrogen stable isotopic analyses, samples were combusted in an elemental analyzer (Carlo Erba NC2500) connected to a Finnigan MAT Delta V mass spectrometer using CONFLO IV. Stable carbon and nitrogen isotope results are expressed in parts per thousand (‰) relative to the VPDB (Vienna PeeDee Belemnite) standard and air, respectively. Based on repeated standard measurements, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were better than $\pm 0.15\text{‰}$.

Results and discussion

History of Lek-Vorkuta peatland based on plant macrofossil analyses

Changes in vegetation during the Holocene development of this peatland are described in Andersson *et al.* (2011) and summarized in Fig. 2. The inception of this peatland was probably through paludification. It subsequently developed into a rich wet fen ~9500 cal a BP (section A1 at the base of the profile) dominated by brown mosses (*Calliergon*). Vegetation in the wet fen then became progressively dominated by vascular plants (mostly sedges) for almost 5000 years (section A2) before the onset of permafrost ca. 2500 cal a BP (radiocarbon date in Fig. 2). The macrofossil analyses suggest that this event took place when frost heave of the peatland surface caused drier, ombrotrophic conditions, which led to radical changes in vegetation. The abundance of *Cenococcum* sclerotia is evidence of drier conditions (Coleman *et al.*, 1989). The system subsequently developed into a peat plateau bog (section B) consisting of alternating stages dominated by mosses (Bs layers, relatively dry) and vascular plants (Br layers, dry). Oksanen *et al.* (2001) reported similar stages in the Holocene development of other peatlands in this region.

TOC, N and H concentrations

TOC concentrations in core LVPS4 + 5B range from 43 to 50%, averaging 45.3 wt% (weight percent) in the bog peat (B) and 47.7 wt% in the fen peat (A) (Fig. 3), which are typical for peat deposits (Vardy *et al.*, 2000; Sannel and Kuhry, 2009). The lowest TOC concentrations appear in bog peat (B) in the *Sphagnum* (Bs)-dominated stages and also at the top of the profile (vascular plant-dominated, Br). Low TOC concentrations in samples from the present peat surface are due possibly to dust deposition (ash contents were not measured) during periods of slow peat accumulation. Peat accumulation ceased ca. 800 a BP (Andersson *et al.*, 2011). Low TOC concentrations near the bottom of the sequence (section A1) may record mixing of peat with underlying mineral subsoil by cryoturbation.

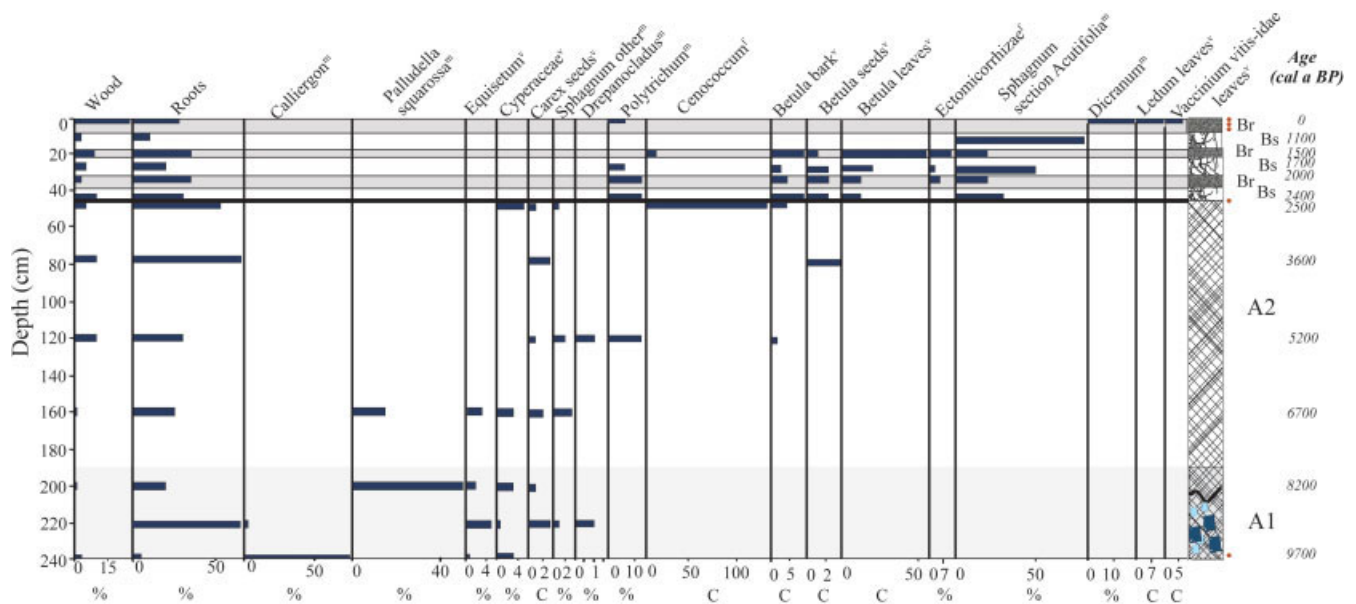


Figure 2. Distribution of plant macrofossils in the LVPS4 + 5B peat sequence reported in Andersson *et al.* (2011) and new macrofossil data at 220 cm depth. Superscripts m, v and f after plant names indicate moss, vascular plant and fungi, respectively. Distributions are expressed as volume percentages of the total sample (%) or as counts per 5 cm³ of analyzed material (C). Zone A corresponds to fen peat deposits and zone B to bog peat deposits. A1, fen deposits dominated by brown mosses; A2, fen deposits dominated by vascular plants; Br, rootlet layers in bog deposits; Bs, *Sphagnum* peat layers in bog deposits. The five dots on the right indicate those depths at which samples were taken for radiocarbon analysis. Approximate ages (cal a BP, based on linear interpolation) are shown. (Plant macrofossil analyses were conducted by P. Kuhry.)

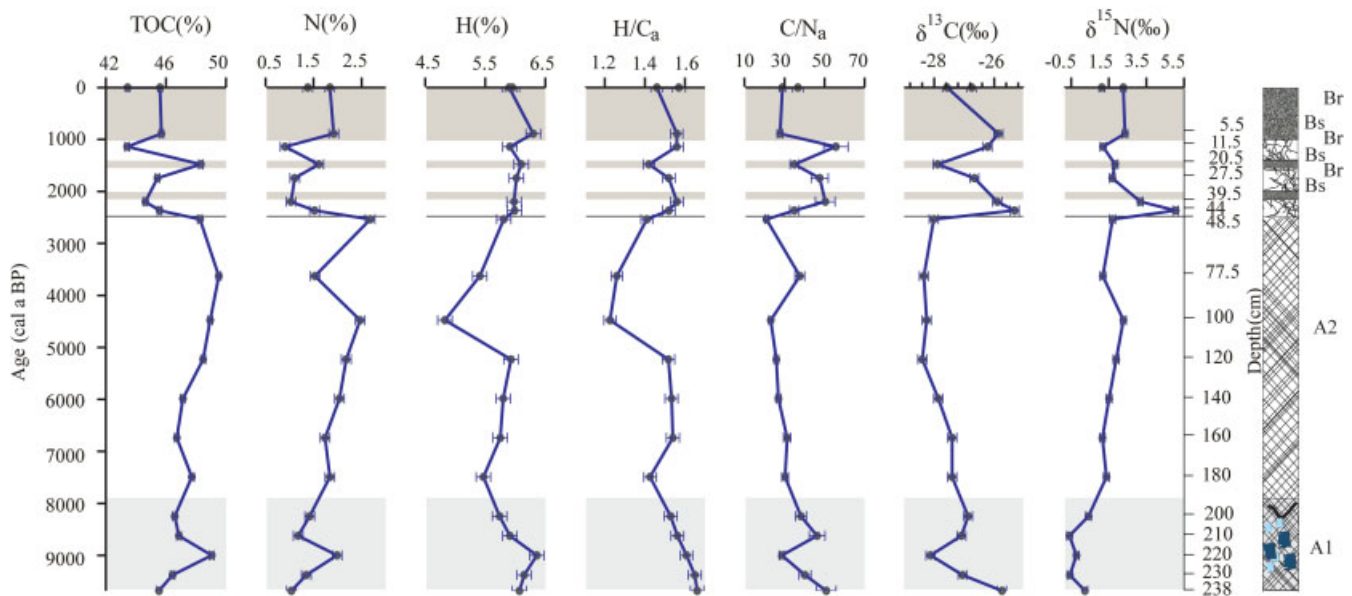


Figure 3. Total organic carbon (TOC) (wt%), total N (wt%), H (wt%), H/C, C/N and bulk peat $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in the Lek-Vorkuta LVPS4 + 5B peat sequence as a function of time (linear interpolation based on calibrated radiocarbon ages). Gray bars indicate the positions of the rootlet layers (Br). Error bars are included. This figure is available in colour online at wileyonlinelibrary.com/journal/jqs.

Nitrogen concentrations range from 0.9 to 2.7 wt%, averaging 1.4 wt% in bog peat (B) and 1.8 wt% in fen peat (A) (Fig. 3). These values are similar to those reported for other permafrost peatlands (Vardy *et al.*, 2000). In general, the patterns of N and TOC concentrations are similar except at 77.5 cm depth. Both parameters differ in the bog (B) versus fen (A) sections, exhibiting consistently lower values in the bog peat. The lowest N concentrations in the bog peat (B) are in the *Sphagnum* layers (Bs) (Fig. 2). In section A2 of the fen peat, N concentrations decrease with depth, coinciding with macrofossil evidence for an increasing abundance of mosses (*Sphagnum* other, *Palludella squarosa*). Low N concentrations also exist at the base of the core in section A1 of the fen peat, which is dominated by brown mosses. An exception to this trend exists at 220 cm depth where vascular plant macrofossils are more abundant (Fig. 2) and increases in concentrations of both TOC and N appear. In general, N concentrations appear to be linked strongly to plant assemblages and the prevailing nutrient status of the peatland at different times during its Holocene development, consistent with the suggestion by Vardy *et al.* (2000) that changes in plant species may control the N content of peat.

Organic matter hydrogen concentrations vary from 4.8 to 6.4%, with a mean of ~ 6 wt% in bog peat (B) and 5.8 wt% in fen peat (A). H concentration decreases in the A2 fen peat, which is dominated by vascular plant macrofossils (Fig. 2). The low H concentration of 4.2% at 100 cm may result from fewer aliphatic components (less mosses) or more lignin-rich compounds derived from vascular plants probably as a result of selective decomposition that produced more lignin-rich residues (Benner *et al.*, 1987). H concentration increases deeper in the profile where macrofossils indicate that mosses coexisted with vascular plants. H concentration peaks at >6 % in fen peat at the bottom of the core in the A1 section where brown mosses dominated under very wet conditions (Fig. 2).

Atomic H/C ratios

The LVPS4 + 5B peat profile consists of alternating successions of mosses and vascular plants with different relative dominances in time. On the basis of mosses being richer in aliphatic

compounds and poorer in lignin compared to vascular plants, the H/C proxy can potentially indicate the botanical and chemical compositions at different depths in the peat profile. However, post-depositional degradation introduces possible complications into the source identification potential of the H/C ratio. Despite being richer in aliphatic components than vascular plants, organic matter from mosses is not expected to decay faster, but slower, than organic matter from land plants. An explanation for this apparent contradiction exists in the observations of Karunen and Ekman (1982) who reported that shoots of *Sphagnum fuscum* become more resistant to decay during senescence because of the biosynthesis and accumulation of aliphatic lipid-derived polymers that resist degradation. Furthermore, many bryophytes contain large concentrations of phenolic compounds in their cell walls (e.g. Erickson and Miksche, 1974; Verhoeven and Liefveld, 1997), which together with non-polar compounds increase the recalcitrance of bryophyte organic matter by inhibiting microbial breakdown and making cell walls impenetrable to fungal hyphae (Verhoeven and Liefveld, 1997; Turetsky, 2003). Hence, bryophyte organic matter decomposes more slowly than vascular plant material. However, the question of whether lignin exists in bryophytes remains controversial. Lignin-like compounds have been detected in the cell walls of some species (Erickson and Miksche, 1974; Edelman *et al.*, 1998), but conclusive evidence remains lacking, even though Siegel (1969) reported the presence of true lignin in the giant mosses *Dawsonia* and *Dendrologotrichum* from New Zealand.

H/C ratios in the LVPS4 + 5B profile range from 1.27 to 1.66 (Fig. 3) and in the bog peat (B) values cluster around a ratio of 1.6, which is close to the H/C ratio of 1.67 typical for cellulose (Kracht and Gleixner, 2000; Sevilla and Fuentes, 2009). H/C ratios of ~ 1.6 occur in peat layers where mosses are abundant, whereas the rootlet layer (Br) at 20.5 cm in which *Betula* is dominant has the lowest H/C ratio of 1.4 (Fig. 3). The range of H/C values in fen peat (A) suggests that differences exist in the preservation of the organic matter with depth in this zone. The macrofossil content in the upper part of the fen peat (A2) is mainly dominated by vascular plants (*Carex* and *Betula*), and H/C ratios decrease to a minimum of 1.27 (100 cm, no macrofossil information available), which is similar to the ratio

reported for lignin compounds (Kracht and Gleixner, 2000). At this depth, this portion of the peat profile also has the lowest H concentration. The values of these geochemical proxies are consistent with the absence of recognizable plant macrofossil residues in this zone, indicating that organic material is highly degraded. The relative contribution of lignin from *Carex* and *Betula* cannot be determined from these data, but low H/C ratios of this zone may be an indication of significant contributions of aromatic structures from decaying remains of herbaceous and woody material. In the lower part of the A2 fen deposit where vascular plants and mosses coexisted (Fig. 2), H/C ratios increase to 1.6. The highest H/C ratios (1.61–1.66) exist at the bottom of the peat profile in the A1 fen peat in which macrofossil content is dominated by brown mosses that probably accumulated under very wet conditions.

In general, the lowest H/C ratios are present in the degraded upper part of the fen peat (A2) where *Carex* and *Betula* remains (Fig. 2) are most abundant, whereas the highest H/C ratios seem to be associated with the presence of mosses in two areas: (i) in the bog peat (Bs) section that developed at the onset of permafrost, and (ii) under wetter anoxic conditions in A2 and A1 of the fen peat.

These observations suggest that the greater abundance of aliphatic structures in mosses is a consequence of either better preservation of organic matter under permafrost or wetter conditions, or is the aliphatic product of senescence in mosses as suggested by Karunen and Eckman (1982). Moreover, Bambalov (2011) reported that during humification aliphatic fragments of lignin in sedges become more abundant than in the original plant, suggesting that degradation of lignin in sedges also produces aliphatic structures. However, instead of increased evidence of aliphatic structures, we found low H/C ratios similar to those of lignin at 80–100 cm in the peat sequence where macrofossils of vascular plants, including *Carex*, were most abundant and heavily degraded. This distribution could also be the result of selective degradation of aliphatic compounds in vascular plant debris that produces lignin-rich residues. Nonetheless, the observed trends in H/C ratios probably also reflect the inherent resistance of mosses to decay.

Atomic C/N ratios

The C/N ratios in the Lek-Vorkuta peat sequence range from 20 to 60 (Fig. 3). Values are highest in the bog peat (B) dominated by *Sphagnum* section *Acutifolia*. The underlying fen peat (A) has lower C/N ratios (mean ~30) that slowly increase towards the bottom of the profile.

The main source of N in ombrotrophic peatlands is atmospheric deposition. In these bogs, *Sphagnum* mats respond quickly to N loading, retaining much of the deposited N (Vitt *et al.*, 2003) before it reaches the anaerobic zone where denitrification occurs (Woodin and Lee, 1987). In contrast, vascular plants depend on nutrients released during organic matter decomposition. Thus, *Sphagnum* can restrict nutrient supply to vascular plants through interception of nutrients delivered by atmospheric deposition. Moreover, the recalcitrance of *Sphagnum* tissue minimizes decomposition, which further restricts the availability of N to vascular plants via SOM degradation (Limpens *et al.*, 2006). Changes in the C/N ratios in the bog peat (B) and in particular within the *Sphagnum* peat layers (Bs) may reflect preferential loss or translocation of N, which increases C/N values (Kuhry and Vitt, 1996; Wieder *et al.*, 2010) (Fig. 3). However, the C/N ratios in the fen peat A2 zone seem to be largely uniform, reflecting the continuous proportional decreases with depth in the concentrations of TOC and N within this zone. The lower C/N ratios in zone A2 relative

to the bog peat (B) may indicate that the fen peat is more degraded and has lost proportionally more C than N over time or they may be the consequence of the sections containing different plant assemblages.

C/N ratios increase gradually with depth throughout the fen peat, with the highest values being in the lower fen peat (A1) where brown mosses were dominant under very wet conditions (Fig. 2). An exception exists at 220 cm in the unit where the C/N ratio decreases and macrofossil data show that vascular plants were more abundant than mosses. H/C ratios also increase with depth in the A2 and A1 fen zones, coincident with an increased abundance of mosses, probably because of greater proportions of aliphatic compounds associated with mosses. High C/N and H/C ratios in the bog peat (B) and in the A2 and A1 fen peat probably reflect better preservation of organic matter owing to permafrost or to wetter and anoxic conditions in the fen peat before the onset of permafrost. However, the ratios also may be recording biogeochemical processes related to the cycling of C and N that differ for mosses and vascular plants in peatlands. For example, the H/C ratio might reflect the aromatic versus aliphatic biochemical contributions of different plant assemblages. Higher values of this ratio seem to be associated with the presence of mosses and/or their senescence, an interesting process that makes their organic matter more resistant to decay. Higher values of this ratio were related to vascular plant debris in the range of lignin. As another example, high C/N ratios may suggest preferential translocation of N relative to C into mosses, yielding higher values associated with better preserved material.

It is difficult to establish conclusively whether the observed changes in elemental proxies are caused predominantly by differences in biochemical composition of the plant assemblages, their particular decay processes or economies in use of C and N. Moreover, it is uncertain to what extent paleoenvironmental conditions subsequently alter these proxies. Distinguishing biochemical and environmental aspects is challenging because of their related impact on plant assemblages in peat profiles such as the one at Lek-Vorkuta. Results from a specific horizon in this profile serve as an illustration of the complexity of this issue. At 220 cm depth, vascular plants dominated, generating an abrupt decrease in the C/N ratio, but the H/C ratio remained high (Fig. 3). It cannot be determined conclusively whether these changes resulted from increased contributions of organic matter from mosses (mostly *Drepanocladus*) and/or their senescence, or as a consequence of wet conditions enhancing the preservation of organic matter.

$\delta^{13}\text{C}$ values of organic matter

The $\delta^{13}\text{C}$ values for organic matter in the LVPS4 + 5B peat sequence range from -28.4 to -25.3‰ (Fig. 3) and the average value is -27.1‰ . Fluctuations in $\delta^{13}\text{C}$ values are greater in the bog (B) than in fen (A) peat, but all values are within the range generally associated with C_3 peat-forming plants (Ménot and Burns, 2001). The average $\delta^{13}\text{C}$ value of fen peat (A) is $\sim 1\text{‰}$ more negative than bog peat (B), and there is a notable positive shift of 2.7‰ in $\delta^{13}\text{C}$ values at the transition from fen to bog (44–48.5 cm depth). The $\delta^{13}\text{C}$ values of bulk peat display an overall increasing trend with depth, similar to the SOM stable isotope values reported by Hornibrook *et al.* (2000) for a temperate zone peat bog in Canada, but opposite in direction to the values reported by Oksanen *et al.* (2001) for the Rogovaya River peat plateau in the Russian Arctic. The positive shift in $\delta^{13}\text{C}$ values with depth in the Lek-Vorkuta peatland appears to be related to changes in vegetation. The more negative $\delta^{13}\text{C}$ values in the bog peat (B) are associated with vascular plant remains (e.g. -27.9‰ at 20.5 cm dominated by *Betula*),

whereas the more positive values occur where *Sphagnum* mosses are dominant (Bs, Fig. 2). These differences in $\delta^{13}\text{C}$ values probably result from differences in the presence and abundance of key biochemical components that comprise peat-forming plants. For example, the cell walls of vascular plants are composed mainly of lignocellulose whereas those of mosses are composed primarily of cellulose (Benner *et al.*, 1987; Kracht and Gleixner, 2000).

The positive shift in $\delta^{13}\text{C}$ values from -28.0 to -25.3‰ at 48.5–44 cm is associated with permafrost aggradation ca. 2500 cal a BP as recorded in plant macrofossils (Fig. 2). Frost heave aerated the peat in the upper fen deposit (A2), leading to aerobic decay of that material. An abundance of *Cenococcum* fungal sclerotia at 48.5 cm also is indicative of drier conditions (Coleman *et al.*, 1989). The shift in soil moisture and aeration driven by permafrost aggradation caused a change in vegetation from vascular plant (sedge)-dominated assemblages (upper part A2) to *Sphagnum* section *Acutifolia* and *Betula* (B) (Fig. 2).

The $\delta^{13}\text{C}$ values in the deeper fen peat (A) are generally more negative than the bog peat (B) but increase with depth to -25.7‰ in basal layers where brown mosses become dominant (Fig. 2; with the exception of 220 cm depth where vascular plant remains are abundant). Strong correlations between TOC concentrations and $\delta^{13}\text{C}$ values ($R = -0.9$, $n = 12$) and C/N and $\delta^{13}\text{C}$ values ($R = 0.8$, $n = 12$) in the fen peat suggest that $\delta^{13}\text{C}$ values are influenced by the amount and preservation of specific botanical constituents.

Nichols *et al.* (2009) suggested that $\delta^{13}\text{C}$ values of *Sphagnum* in ombrotrophic peatlands are influenced by CH_4 fluxes because methanotrophic bacteria live symbiotically within *Sphagnum* mosses (Raghoebarsing *et al.*, 2005). Methanotrophy appears to provide additional CO_2 to *Sphagnum* via oxidation of CH_4 intercepted as it diffuses across the oxic-anoxic interface in the acrotelm. Methane in wetlands, in particular ombrotrophic peatlands, has very negative $\delta^{13}\text{C}$ values (~ -85 to -55‰ , Hornibrook, 2009), and its conversion to CO_2 provides a potential source of ^{13}C -depleted carbon for *Sphagnum*. Consequently, under wetter conditions higher rates of diffusive CH_4 flux may cause a negative shift in the $\delta^{13}\text{C}$ values of *Sphagnum* biomass. Although methanotrophic bacteria can consume considerable amounts of CH_4 in wetlands (Hanson and Hanson, 1996; Segers, 1998), $\delta^{13}\text{C}$ values of organic matter in the Lek-Vorkuta peatland appear to be minimally influenced by recycling of CH_4 , and the majority of change in peat $\delta^{13}\text{C}$ values with depth is best explained by shifts in vegetation type. The fen peat (A2) below the bog deposit (B) has the most negative $\delta^{13}\text{C}$ values, and the macrofossil assemblage indicates a predominance of vascular plants. The H/C and C/N ratios in this zone suggest that the peat is highly degraded. However, $\delta^{13}\text{C}$ values are similar to the lowest value measured in the bog peat (B) at 20.5 cm where *Betula* was dominant under permafrost conditions. These data support the suggestion by Skrzypek *et al.* (2010) that $\delta^{13}\text{C}$ values of peat are not significantly impacted by diagenesis. The $\delta^{13}\text{C}$ values are more positive in the lower part of the A2 fen deposit at the same depths where macrofossil data indicate that mosses coexisted with vascular plants (Fig. 2) and where H/C and C/N ratios increase. Similar to the bog peat (B), the presence of *Sphagnum* mosses is associated with more positive $\delta^{13}\text{C}$ values. The deepest fen peat (A1) contains the most ^{13}C -enriched organic matter at depths where brown mosses were dominant (*Calliargon*). The $\delta^{13}\text{C}$ values in the A1 deposit are most similar to values measured in *Sphagnum*-rich bog peat (B), which formed after permafrost aggradation. The deep fen peat (A) also has high H/C and C/N ratios, indicating the moss-rich material is well preserved. The negative

$\delta^{13}\text{C}$ value at 220 cm depth is associated with an increase in the abundance of vascular plant remains and is similar to values observed in the upper part of the A2 fen deposit where vascular plants were dominant.

Clymo and Bryant (2008) reported no changes in $\delta^{13}\text{C}$ values of peat to a depth of 7 m in a raised bog, even at depths where $>60\%$ of the original plant material had been lost due to decay. In bogs and fens, much of the plant biomass is metabolized higher in the chain of decay where no significant partitioning of C isotopes is associated with biological degradation. Discrimination of ^{13}C occurs primarily during the terminal stages of anaerobic C mineralization where CH_4 (and CO_2) are produced (Clymo and Bryant, 2008) and the amounts of energy and C cycled at that level are small relative to overall degradation of complex organic matter. The observed changes in $\delta^{13}\text{C}$ values with depth are therefore most probably caused by differences in the relative accumulation of vascular plant and bryophyte remains and the differences that exist in their primary biochemical compositions.

Changes in $\delta^{15}\text{N}$ values

Approximately 95% of the N in peatland ecosystems is contained in dead organic matter (Rosswall and Granhall, 1980). Microbial mineralization of peat slowly makes a small fraction of organic N available to plants. In terrestrial ecosystems, loss of N under anaerobic conditions occurs mainly through microbial denitrification in which NO_3^- is reduced to N_2O and N_2 or through anaerobic ammonium-oxidizing (anammox) bacteria that oxidize NH_4^+ to N_2 using NO_2^- . The latter process has been reported to occur in peat soil, including a permafrost peatland (Humbert *et al.*, 2009; Hu *et al.*, 2011). The roots of aerenchymatous plants (e.g. *Carex*, *Eriophorum*) contribute significantly to N-cycling in wetlands by providing a niche for ammonia- and nitrite-oxidizing bacteria. Nitrate produced in this way can be used subsequently by denitrifying bacteria or taken up directly by plants (Bodelier *et al.*, 1996).

In the Lek-Vorkuta peatland, $\delta^{15}\text{N}$ values of peat range from -0.6 to 5‰ with average values of 2.3‰ and 0.87‰ in bog (B) and fen (A) peat, respectively. A positive shift of $\sim 3\text{‰}$ occurs in the bog deposit (B) immediately above the transition from fen (A2) peat. The excursion in $\delta^{15}\text{N}$ values to 5.5‰ between 48.5 and 44 cm depth (ca. 2500 cal a BP) coincides with permafrost onset (Fig. 2). Frost heave of the peat surface lowered water table levels, allowing aerobic decay of organic matter. Regina *et al.* (1999) demonstrated that lowering of the water table in boreal peatlands increases N_2O fluxes because nitrification is enhanced, which stimulates N mineralization of soil organic matter. Data from the Lek-Vorkuta peatland appear to be in agreement with that observation. An abundance of *Cenococcum* at 48.5 cm depth (Fig. 2) indicates a shift from wet to drier conditions, and during that transition enhanced nitrification would be followed by greater N mineralization, leaving the soil enriched in ^{15}N . The fen peat (A) has low $\delta^{15}\text{N}$ values that further decrease gradually with depth. The $\delta^{15}\text{N}$ value of $\sim 0\text{‰}$ at the base of the peat column where brown mosses are dominant (Fig. 2) is typical for ecosystems that receive low N input from atmospheric deposition (Kracht and Gleixner, 2000; Francioso *et al.*, 2005).

Significant correlations do not exist between $\delta^{15}\text{N}$ values and $\delta^{13}\text{C}$ values or TOC concentrations. However, $\delta^{15}\text{N}$ values in fen peat (A) correlate positively with N concentrations ($R = 0.75$, $n = 12$) and negatively with C/N ratios ($R = -0.74$, $n = 12$), suggesting that under anoxic conditions more positive $\delta^{15}\text{N}$ values are associated with more degraded plant material. The most positive $\delta^{15}\text{N}$ values at 100 cm depth in the fen peat

are associated with low H/C ratios and high N concentrations, consistent with nitrogen in vascular plants being made available primarily through microbial mineralization, which leaves a ^{15}N -enriched lignin residue (Francioso *et al.*, 2005).

Conclusions

Elemental and stable isotope proxies analyzed in soil organic matter from the Lek-Vorkuta peatland provide insight into the complexity of C and N cycling in peatland ecosystems. The geochemical measurements conducted in concert with plant macrofossil analyses proved to be useful for characterizing C and N flow during long-term peatland development, demonstrating in particular key differences that occur in the cycling of these elements and more generally in organic matter in fens and bogs.

Atomic H/C and C/N ratios, supported by plant macrofossil data, are useful indicators of differences in the origin of organic matter, its decay and shifts in the dominant mechanisms of nitrogen allocation reflecting changes in vegetation. The H/C ratio appears to be a sensitive indicator of the aromatic versus aliphatic biochemical composition of plant organic matter. Higher values in the Lek-Vorkuta peat sequence are associated with mosses and/or their senescence, suggesting that peat derived from moss is more resistant to degradation than organic matter from vascular plants. The elemental data also indicate that mosses have a higher capacity than vascular plants to intercept nitrogen.

Changes of $\delta^{15}\text{N}$ values with depth appear to be controlled primarily by N isotope fractionation associated with microbial decomposition of plant detritus and peat. In contrast, changes in $\delta^{13}\text{C}$ values of peat are determined mainly by succession and shifts in composition of dominant plant communities. Diagenesis of peat appears to have had minimal impact on $\delta^{13}\text{C}$ values of organic matter in the Lek-Vorkuta peatland. The effect of the permafrost aggradation that drove the transition from fen peatland to plateau bog at ~ 2500 cal a BP was clearly evident in all elemental and isotopic measurements, confirming the utility of these geochemical proxies for reconstructing the accumulation history and decomposition trajectories of organic matter in global peatland ecosystems.

Given the complex plant assemblage in the peat profile, changes in degradation observed in the elemental and isotopic proxies seem to be related primarily to contributions from specific types of plants. However, important questions remain that need further investigation. Studies on the variability of peat degradation based on a single functional plant will help in this regard.

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Abbreviations. SOM, soil organic matter; TOC, total organic carbon.

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