Soil Chemistry

# Chemical Composition of Soil Organic Matter in a Subarctic Peatland: Influence of Shifting Vegetation Communities

**Anna E. Normand***
Wetland Biogeochemistry Laboratory, Soil and Water Sciences Department, McCarty Hall A, PO Box 110290, University of Florida, Gainesville FL 32611

**Adam N. Smith**
Department of Chemistry, University of Florida, Gainesville, FL 32611

**Mark W. Clark**
Wetland Biogeochemistry Laboratory, Soil and Water Sciences Department, McCarty Hall A, PO Box 110290, University of Florida, Gainesville FL 32611

**Joanna R. Long**
Department of Biochemistry and Molecular Biology

**K. Ramesh Reddy**
Wetland Biogeochemistry Laboratory
Soil and Water Sciences Department
McCarty Hall A
PO Box 110290
University of Florida
Gainesville FL 32611

**Climate change in the subarctic region has increased the rate of inundation of peatlands due to increased temperatures, precipitation, and permafrost thaw. Increased inundation may result in vegetation community shifts, as documented in a subarctic mire near Abisko, Sweden. The wet fen communities have established in former sphagnum areas, and sphagnum colonized in degraded palsa hummocks. At Stordalen mire, we studied the influence of vegetation community on chemical composition of peat soil organic matter (SOM). Vegetation and soil samples were obtained along a hydrologic gradient with representative communities: palsa, sphagnum, and fen. Soil organic matter chemical composition indicated shifts in vegetative communities. Total N and N isotope signatures in fen soils showed characteristics of sphagnum and palsa communities at >6-cm depth, and sphagnum soil profile signatures shifted from sphagnum to palsa properties at a 20-cm depth. Soil chemical composition measured by Fourier Transform Infrared (FTIR) spectroscopy and $^{13}$C Nuclear Magnetic Resonance (NMR) spectroscopy showed increasing recalcitrant C (alkyl and aromatic) in palsa soil. Sphagnum soil profiles sustained labile organic C (O-alkyl) until 15 cm then shifted to humified soil, and fen soil profiles showed areas of sphagnum and palsa signatures. Furthermore, the strong relationship between functional group C (O-alkyl and alkyl) and total N demonstrated that soil N is an effective indicator of peat decomposition. Our results identified change points in soil chemical composition in regards to N content and C functional group which highlights the importance of historic vegetation community on chemical composition of peat soils.**

Abbreviations: ATR, attenuated total reflectance; $^{13}$C ssNMR, solid state $^{13}$C nuclear magnetic resonance; CPTOSS, cross polarization with total sideband suppression; DOM, dissolved organic matter; FTIR, Fourier Transform Infrared; GHG, greenhouse gases; MAS, magic angle spinning; NMR, Nuclear Magnetic Resonance; SOM, soil organic matter.

## Core ideas:

- **Soil organic matter chemical composition highlighted the inputs of varied vegetation communities in the past.**
- **Soil N is an indicator of peat decomposition based on relationship of functional group C and total N.**
- **Future surveys of soil organic matter biogeochemical parameters and C chemical composition should be pursued.**

Peatlands have accumulated large pools of SOM after the last glaciation as plant biomass production has exceeded decomposition of organic matter (Gorham, 1991). Organic matter accumulation is the result of waterlogged conditions where decomposition of senesced vegetation is slow due to anoxic conditions and compounded by cool and acidic environment (Laiho, 2006). Peatland ecosystems are mostly in the boreal and subarctic areas and cover approximately 4 million km$^2$ or 3% of the world's land area (Frolking et al., 2011; Page et al. 2011). Peatland soils contain approximately ~450 to 500 Pg of C—larger than any C stock in the terrestrial biosphere (Gorham, 1991; Bridgham et al., 2006). Destabilization of this large and potentially vulnerable pool of peatland C could have a major impact on climate through emissions of greenhouse gasses (GHG) and export of dissolved organic matter (DOM), thus transforming these ecosys-

Soil Sci. Soc. Am. J. 81:41–49
doi:10.2136/sssaj2016.05.0148
Received 16 May 2016.
Accepted 25 Oct. 2016.
*Corresponding author (evangeline@ufl.edu).

tems from a C sink to a C source (Fenner et al., 2007; Limpens et al., 2008; Frolking et al., 2011).

Climate change over the next century will affect vegetation communities in peatlands (Flanagan, 2013). External drivers such as irregular patterns in precipitation and temperature may influence diversity of vegetation species composition and biogeochemical processes regulating SOM decomposition (Breeuwer et al., 2008; Lamentowicz et al., 2009). Particularly in the subarctic region of Europe, climate change is predicted to increase temperature more rapidly than the global mean, increase annual mean precipitation, and decrease of permafrost by 37 to 81% (Ciais et al., 2013). These climate drivers can potentially result in increased frequency of inundation and consequently shift vegetation communities more suited for saturated soil conditions in peatlands (Kokfelt et al., 2010). For example, changes in climate and vegetation communities have already been observed in a subarctic mire ecosystem near Abisko, Sweden (Johansson et al., 2006). Three vegetation community types dominate the system: 1. permafrost sites consisting of drained, raised palsa areas with woody herbaceous vegetation; 2. intermediate thaw features with *Sphagnum spp.* where the water table is close to the surface; and 3. wet fen dominated by *Eriophorum spp.* where the ground completely thaws (Bäckstrand et al., 2010). During the past 40 years, the wet fen communities have established in former sphagnum areas, and sphagnum has colonized in degraded palsa hummocks (Malmer et al., 2005). The altered hydrologic regime selecting for vegetative communities may dictate the quantity and quality of litter inputs and subsequent SOM composition and decomposition (Bauer, 2004; Frolking et al., 2010).

Peatland response to climate change depends on the chemical composition of vegetative inputs and legacy peat (Feng et al., 2008; Frolking et al., 2011). In addition to environmental conditions, vegetation litter inputs and subsequent SOM development have been shown to have a dominant effect on C cycling (Laiho, 2006; Treat et al., 2014). Inundation change, whether towards a drier or wetter system, can shift entire vegetation community distributions, thus altering the organic matter inputs (Price and Whitehead, 2004; Talbot et al., 2010). Limited information is available on the consequence of vegetation changes resulting in contrasting C composition inputs and storage in peatlands. Chemical composition of SOM at a molecular level and its relationship to decomposition is especially vague. Soil organic matter composition throughout the upper soil profile is dictated by litter inputs and is an important regulator of soil loss, GHG emissions, and DOM export to adjacent aquatic systems (Lafleur et al., 2005; Nilsson and Öquist 2009).

Application of FTIR and solid state $^{13}$C NMR ($^{13}$C ssNMR) provide advanced understanding of SOM composition (Simpson et al., 2011; Derenne and Nguyen, 2014). Fourier Transformed Infrared spectroscopy and $^{13}$C ssNMR can depict soil chemical composition and the likely implications of C cycling in wetlands ecosystems with specific peat chemical composition (Wright et al., 2011; Leifeld et al., 2012). Specific C moieties are believed to have varied effects on SOM cycling and biogeochemical processes (Clemente et al., 2013; Marin-Spiotta et al., 2014). Carbon−13 Solid State NMR identifies the organic functional groups in SOM that vary in molecular composition and microbial utilization: carboxyl, aromatic, O-alkyl, methoxyl, and alkyl based on chemical peak shifts (Knicker, 2011; Simpson et al., 2011). Fourier Transform Infrared spectroscopy also identifies basic C functional groups specifically carbohydrates and aliphatics (Baker et al., 2014). Carbohydrates generally enhance decomposition; therefore, the O-alkyl functional group may be useful in predicting respiration rates (Leifeld et al., 2012; Tfaily et al., 2014). While oxygen-rich moieties have been shown to diminish during peat formation and through the soil profile, lignin and polyphenols (aromatic and phenolic functional groups) and microbial derived hydrophobic aliphatic (alkyl) species disproportionally accumulate under anaerobic conditions (Baldock et al, 1997; Clemente et al., 2013). Phenolic compounds are believed to suppress decomposition under anaerobic conditions, but phenolics may degrade enzymatically through phenol oxidase under aerobic conditions (Freeman et al., 2004). Aliphatic functional groups are known to be a determinant of humification, yet the role of aliphatic compounds in mineralization processes in peat is unclear (Baldock et al., 1997; Clemente et al., 2013).

In this study, we examined the SOM chemical composition as influenced by vegetation types across a hydrology gradient: fen, sphagnum, and palsa. The objective of this study was to determine the effect of shifting vegetation inputs due to increased inundation on peatland SOM composition. Our hypothesis was that the hydrologic regime selecting for vegetative communities will dictate legacy vegetation shifts and change the chemical composition of SOM.

## MATERIALS AND METHODS

### Site Description

Stordalen mire (68°20′N, 19°03¢E, altitude 351 m) is a 25-km$^2$ subarctic peatland located in the subalpine region near Abisko, Sweden (Fig. 1). Annual average precipitation in the region has increased from 282 mm (1913–1930) to 339 mm (1990–2013). Also, annual average temperatures recorded at the Abisko Scientific Research Station have increased from −1.0°C year average (1913–1930) to 0.2°C (1990–2013) resulting in mean temperatures above 0°C in the past decade (Nordklim dataset 1.0 by Tuomenvirta et al., 2013 and Abisko Research Station). Stordalen mire is underlain by discontinuous permafrost which is experiencing ongoing permafrost thaw intensified by increasing temperatures (Malmer et al., 2005). The heterogeneous moisture regimes with specific nutrient levels select for different vegetation types (Fig. 1; Bäckstrand et al., 2008). Permafrost zones contain elevated, drained palsa areas with diverse vegetation cover: dwarf shrubs, lichens, mosses, and herbaceous vegetation (Bäckstrand et al., 2010). Along the thaw gradient, *Sphagnum spp.* dominates where water table fluctuates close to the surface. Wet, minerotrophic depressions consisting of *Erophorum angustfolium* and *Carex spp.* are inundated and without permafrost. These three vegetation community types dominate the system and are referred to as palsa, sphagnum, and fen. Vegetation surveys and satellite images from 1970 to 2000 have shown an expanse of communities better suited for increased innundation (Johansson et al., 2006). Increased inundation of the system is believed to be from increased annual precipitation and degradation of the discontinuous permafrost from increased temperatures (Bäckstrand et al., 2010).

## Sampling

In June 2013, palsa, sphagnum, and fen sites were sampled for peat soil along a 26-m hydrology and nutrient gradient. Soils at the sampling sites are classified as Typic Cryofibrists (Bliss et al., 1981). Three cores of soil profiles were sampled at each site within 1- to 2-m distance from each other where the vegetation composition was representative of the sites of Bäckstrand et al. (2010). A push corer (12 cm in diam.) was used to retrieve soil of 40-cm depth or until reaching frozen soil at 30 cm. Soil cores were sectioned into 2-cm depth increments using a serrated edge knife totaling 292 sectioned samples. Live and dead vegetation, and litter above the soil core were obtained if available. Soil and vegetation samples were transported to the Abisko Research Station for immediate processing.

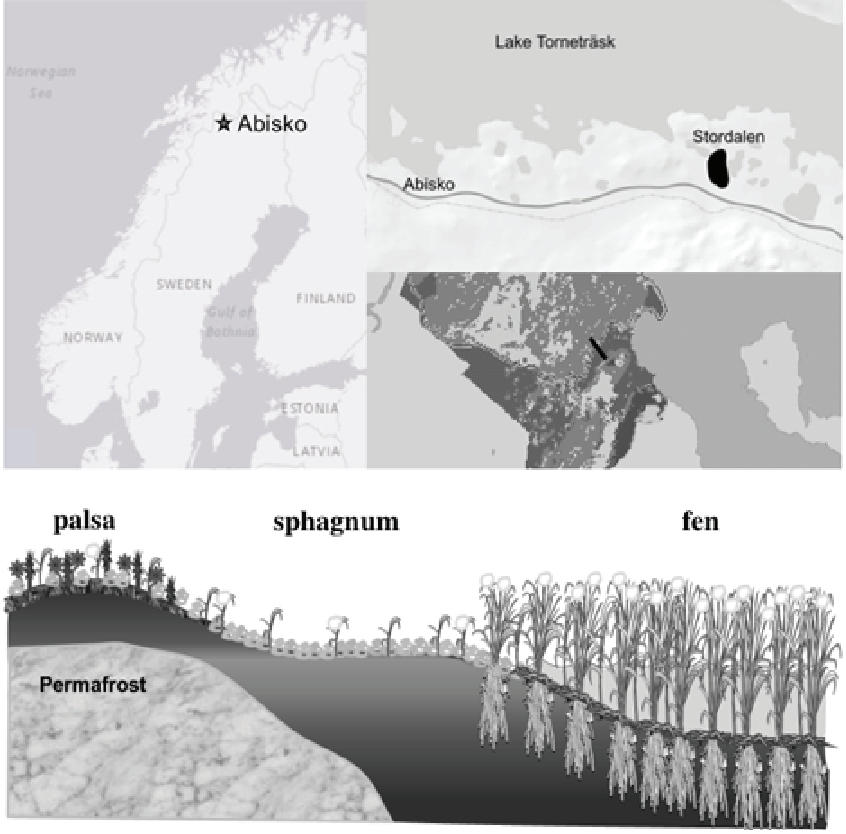

**Fig. 1. Stordalen Mire is 11 km from Abisko, Sweden in the subarctic region of Scandinavia. Location of the sampling transect (solid line) in Stordalen Mire and representation of Stordalen vegetation communities across the hydrology gradient: palsa underlain by permafrost, ombrotrophic sphagnum, and minerotrophic fen.**

## Bulk Physical and Chemical Properties

Soil bulk density and pH were measured using methods described by Reddy et al. (2013). Soil and vegetation samples were air dried at 30°C in a drying room with a fan until constant weight. Dried vegetation and soil samples were mailed to University of Florida for further analysis. Air-dried soil and vegetation samples were ground using a Wiley Mill. Total C and N, and stable isotope ratios of $\delta^{13}C$ and $\delta^{15}N$ were determined simultaneously using a Costech model 4010 elemental analyzer (Costech Analytical Industries) coupled to a Finnigan MAT DeltaPlusXL mass spectrometer (CF-IRMS, Thermo Finnigan) via a Finnigan Conflo III interface. Mean values and standard deviations for each measurement were calculated ($n = 3$).

## Spectroscopic Analyses

**Fourier Transformed Infrared spectroscopy.** Spectral characterization of peat samples was performed by diamond attenuated total reflectance FT-IR spectroscopy using a PerkinElmer Spectrum 100 FT-IR spectrometer fitted with a CsI beam splitter and a deuterated triglycine sulfate detector. Transmission-like spectra were produced via an attenuated total reflectance (ATR) accessory made from a composite of zinc selenide (ZnSe) and diamond, with a single reflectance system. Ground peat samples from 2 cm peat segments were placed directly on the crystal and force was applied to ensure good contact between the crystal and the sample. Spectra were acquired at a 4-$cm^{-1}$ resolution (wavenumber) over the range 4000 to 640 $cm^{-1}$. The spectra were corrected for the ATR to allow for differences in depth of beam penetration at different wavelengths, and then baseline corrected, with the instrument software. Spectral absorbance values were identified based on assignments by Tfaily, et al. (2014): aliphatic (2920 $cm^{-1}$) and carbohydrate (1030 $cm^{-1}$).

**$^{13}C$ ssNMR Spectroscopy.** Samples of ground vegetation, litter, and soil were analyzed by magic angle spinning (MAS) $^{13}C$ ssNMR spectroscopy. Live and dead vegetation, below ground biomass, and detritus at each site were composited from three replicate cores. Select peat cores were analyzed based on FT-IR results. Soil was composited into 4-cm segments. Magic angle spinning $^{13}C$ ssNMR experiments were carried out on a Bruker 500 MHz Avance III spectrometer equipped with a 3.2-mm E-free H/C/N probe. Samples were packed into zirconia rotors with Kel-F drive caps and spun to 8 kHz at 233 K. Magic angle spinning $^{13}C$ ssNMR spectra were collected utilizing a Cross Polarization with Total Sideband Suppression (CPTOSS) pulse sequence (Dixon et al., 1982). A 2.5 $\mu s$ $^{1}H$ $\pi/2$ pulses followed by 1.5-ms ramped CP pulses at 100 kHz ($^{1}H$) and 55 kHz ($^{13}C$) was used. $^{13}C$ $\pi$ pulses were applied at 125-$\mu s$ intervals for sideband suppression. 100 kHz of $^{1}H$ decoupling was employed during the 40-ms signal acquisition time. The 4096 transients were collected for each experiment with a recycle delay of 3 s. The

MAS $^{13}C$ ssNMR spectra were referenced using an external adamantane reference and spectral regions were integrated to determine the percentage of contribution of each C functional group in the sample based on assignments from Knicker (2011): alkyl (0–45 ppm), methoxyl (45–60 ppm), O-alkyl (60–90 ppm), di-O-alkyl (90–110 ppm), aromatic (110–140 ppm), phenolic (140–160 ppm), and carboxyl (160–220 ppm). The percentage of C functional group was converted to g functional group C kg$^{-1}$ sample using total C values of the vegetation and soil samples.

## Statistical Analyses

Pearson's correlations between soil properties were done with pairwise analysis. Pearson's correlation was used to measure of the strength and direction of association between soil N properties and FTIR ratios and NMR functional groups. Statistical analyses were performed with the statistical package JMP (Version 4.04, SAS Institute), with significance set at $\alpha = 0.05$. Vegetation and soil properties were averaged between replicate cores: values reported are means followed by values that are standard deviations.

# RESULTS

## Bulk Physical and Chemical Properties

Soil pH ranged from 3.4 to 4.1 at the palsa site as compared with 4.0 to 4.7 at the fen site. Bulk density was low in the upper fen and sphagnum soil (ranging from 0.06–0.11 g cm$^{-3}$) and increased with depth to 0.18 g cm$^{-3}$ (Fig. 2a). Palsa bulk density ranged from 0.20 to 0.33 g cm$^{-3}$. Carbon content of live vegetation and soil ranged from 385 to 515 g C kg$^{-1}$ among all three plant communities, while N content varied in vegetation and soil profiles from 5 to 30 g N kg$^{-1}$ (Fig. 2b and 2c). Nitrogen content was highest in live fen vegetation (13.8 ±

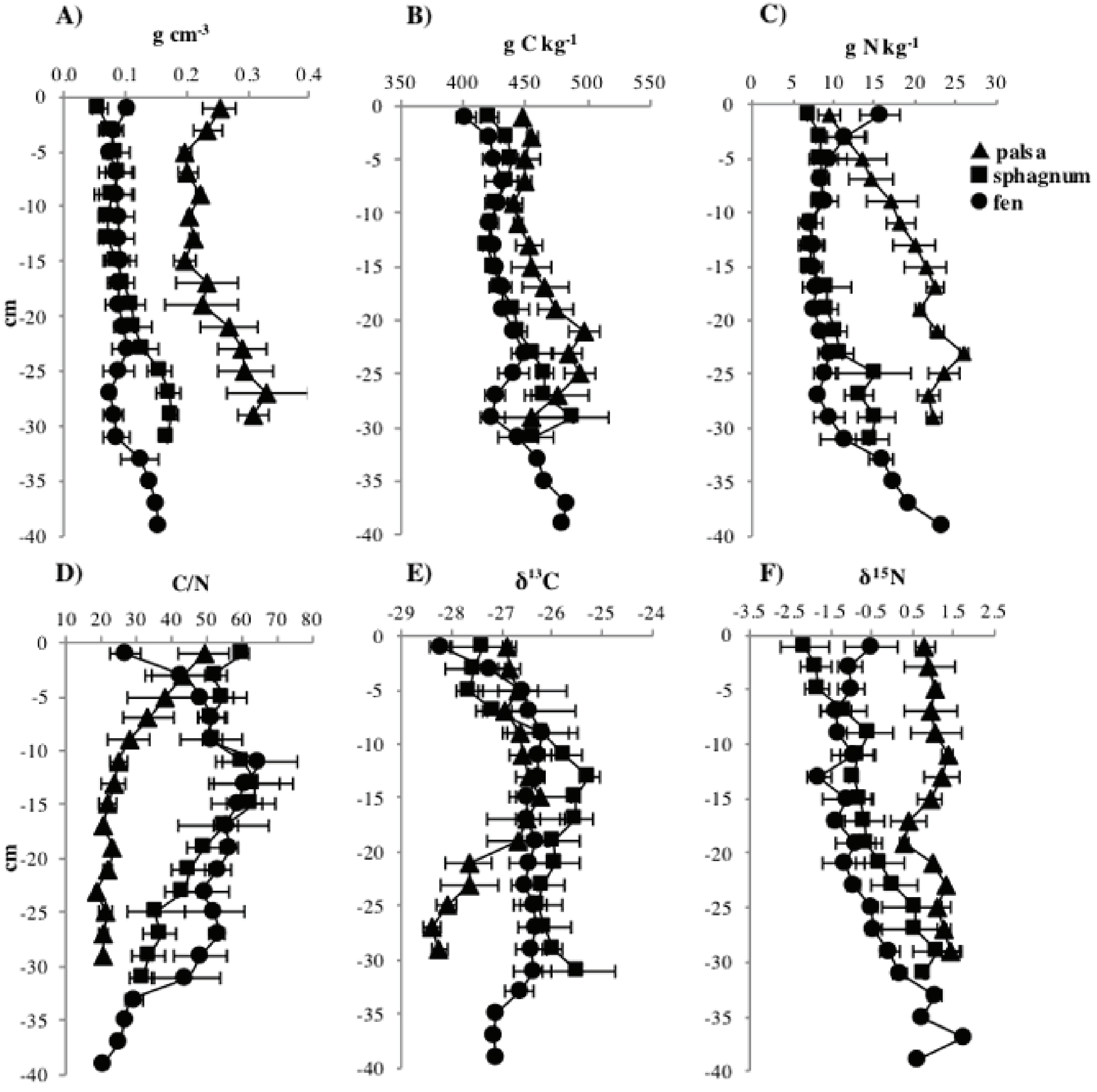

**Fig. 2. Soil profile biogeochemical properties at the three vegetative communities: ▲ palsa, ■ sphagnum, and ● fen. (A) estimated bulk density; (B) mass of total C; (C) mass of total N; (D) C/N molar ratio; (E) $\delta^{13}C$ isotope concentration; and (F) $\delta^{15}N$ isotope concentration.**

0.5 g N kg$^{-1}$) compared with palsa (11.6 ± 0.9 g N kg$^{-1}$) and sphagnum (6.6 ± 0.1 g N kg$^{-1}$) vegetation (Table 1). Nitrogen content in palsa, fen, and sphagnum soil profiles steadily increased with depth. Nitrogen was lower in the upper sphagnum soil (8.0 ± 1.8 g N kg$^{-1}$ at 0–20 cm) but increased to 14.7 ± 3.5 g N kg$^{-1}$ at 30 to 32 cm. Fen soil had higher N from 0 to 6 cm (12.2 ± 4.2 g N kg$^{-1}$); however, fen soil from 6 to 28 cm had a similar amount of N (8.2 ± 1.7 g N kg$^{-1}$) compared with 0 to 20 cm from sphagnum profile.

Vegetation samples (live, dead, below ground, and detritus) $\delta^{13}$C mean values ranged from −26.7 to −28.4‰ reflecting the composition of C3 plants of peat mires (Table 1; Andersson et al., 2012; Krüger et al., 2014). The palsa soil did deplete in $\delta^{13}$C at ~15 cm to −26.2 ± 1.1 (Fig. 2e). Enrichment of $\delta^{15}$N changed during the decay continuum from live vegetation to 0- to 2-cm soil for palsa and fen, but $\delta^{15}$N was stable for sphagnum (−2.2 ± 0.7‰). The palsa live and dead vegetation were depleted at −1.6 ± 0.3‰. The palsa below ground root mat (−0.5 ± 0.1‰) and 0- to 2-cm palsa soil (0.8 ± 0.3‰) showed more enriched signatures than the aboveground vegetation. The $\delta^{15}$N enriched values ranged from −0.4 to 2.0‰ through the palsa profile (Fig. 2f). The initially N enriched fen live vegetation (2.3 ± 0.8‰) depleted to −0.5 to −1.8‰ in the upper soil profile. The $\delta^{15}$N profiles of sphagnum and fen soils ranged from −0.5 to −2.2‰ in the upper soil profile, then became steadily enriched (ranging from 0.3 to 1.8‰).

### Organic Carbon Functional Groups

Organic C functional groups were determined by both FTIR and $^{13}$C ssNMR. Fourier Transformed Infrared spectroscopy provides a rapid assessment of SOM composition supported by C functional groups. Carbon functional groups absorb specific infrared wavelengths depending on their chemical bonds (Baker et al., 2014). Polysaccharide C-OH bonds absorb 1030 cm$^{-1}$ wavelength and aliphatic $CH_2$ and $CH_3$ bonds absorb 2090 cm$^{-1}$ wavelength (Tfaily et al., 2014). The absorbance intensity at specific wavelengths also depends on the amount of sample C probed by infrared radiation.

The ratio 2090 cm$^{-1}$:1030 cm$^{-1}$ (aliphatic/polysaccharide) expresses an indication to the extent of SOM decomposition and transformation (Tfaily et al., 2014). Higher ratios correspond to increased humification of soil and are comparable with the alkyl/O-alkyl ratios that may be obtained from $^{13}$C ssNMR spectra (presented in the following paragraph). The palsa soil showed steady increase in humification through the soil profile from 0.9 ± 0.1 at 0 to 2 cm to 1.8 ± 0.4 at 28 to 30 cm (Fig. 3a). The sphagnum soil maintained a consistent humification ratio (ranged from 0.6–0.9) in the upper profile. Deeper in the sphagnum soil profile, the humification ratio steadily increased to 1.1 ± 0.2 at 28–30 cm. The fen soil also had consistent humification ratio to a depth of 30 cm (ranging from 0.6–1.1). At depths 30–40 cm, the humification ratio steadily increased in fen soil to 1.6. Total N and C/N ratio versus the ratio of aliphatic (2920 cm$^{-1}$) to polysaccharide (1030 cm$^{-1}$) showed moderate positive Pearson's correlations with $r$ of 0.66 and 0.45, respectively.

**Table 1 Vegetation characteristics from the vegetation communities across the hydrology gradient. Abbreviations are L - live, D - dead, BG - below ground, and Dt – detritus. Mean values are followed by standard deviation.**

| | C | N | C/N | $\delta^{13}$C | $\delta^{15}$N |
|---|---|---|---|---|---|
| | g C kg$^{-1}$ | g N kg$^{-1}$ | | | |
| Palsa | | | | | |
| L | 461 ± 10 | 11.6 ± 0.9 | 40 ± 4 | –28.4 ± 0.5 | –1.5 ± 0.6 |
| D | 442 ± 5 | 6.7 ± 0.7 | 68 ± 6 | –27.1 ± 0.7 | –1.7 ± 0.1 |
| BG | 447 ± 2 | 9.4 ± 0.7 | 48 ± 3 | –27.0 ± 0.4 | –0.5 ± 0.1 |
| Sphagnum | | | | | |
| L | 414 ± 2 | 6.6 ± 0.1 | 63 ± 1 | –26.7 ± 0.6 | –2.3 ± 0.2 |
| fen | | | | | |
| L | 436 ± 2 | 13.8 ± 0.5 | 32 ± 1 | –28.1 ± 0.5 | 2.3 ± 0.7 |
| D | 433 ± 5 | 6.7 ± 0.2 | 65 ± 3 | –28.3 ± 0.7 | 0.6 ± 0.4 |
| BG | 432 ± 8 | 10.1 ± 0.4 | 43 ± 2 | –27.7 ± 0.7 | 1.3 ± 0.9 |
| Dt | 443 ± 20 | 10.1 ± 0.7 | 45 ± 5 | –28.4 ± 0.6 | –0.4 ± 1.3 |

Carbon-13 Solid State NMR probes all $^{13}$C atoms in the organic matter sample and differentiates between the chemical environments of the C atoms (Simpson et al., 2011). The resulting spectrum can be partitioned to different C functional groups (Knicker, 2011). Carbon-13 Solid State NMR analysis determined the g functional group C kg$^{-1}$ of sample through the decay continuum. The O-alkyl region dominated the spectrum of Stordalen vegetation and 0- to 2-cm soil from all vegetation communities (ranging from 222 to 316 g functional group C kg$^{-1}$; Fig. 4). Throughout the soil profile, the contribution of carboxyl, aromatic, and methoxyl C was low (ranging from 4 to 68 g functional group C kg$^{-1}$; Fig. 3b, 3c, and 3d). In the palsa soil, O-alkyl C steadily depleted with depth from 281 to 90 g functional group C kg$^{-1}$ whereas alkyl C increased from 64 to 272 g functional group C kg$^{-1}$ (Fig. 3b). Sphagnum soil from 0 to 18 cm was dominated by O-alkyl C (299 ±16 g functional group C kg$^{-1}$); however, beginning at 20 cm in sphagnum soil profile, O-alkyl C decreased to 212 g functional group C kg$^{-1}$ and alkyl C increased to 168 g functional group C kg$^{-1}$ (Fig. 3c). Pearson's correlations showed strong relationships with ssNMR functional groups and total N (Fig. 5; $r = -0.78$ for O-alkyl C and $r = 0.83$ for alkyl C, $p < 0.0001$, $n = 26$).

## DISCUSSION

### Shifting Vegetative Communities and Soil Organic Matter Chemical Response

Accumulation of organic matter results in storage of nutrients which are transformed or released during decomposition. Both vegetation inputs and hydrologic conditions control the cycling of organic matter and resulting nutrient release. The SOM chemical composition throughout the palsa soil profile represents highly humified soil due to aerobic decomposition and persistence of alkyl C from woody vegetation (Pengerud et al., 2013; Krüger et al., 2014). The palsa live vegetation had the highest alkyl C content compared with fen and sphagnum live vegetation likely due to waxy lipids and lignin compounds from

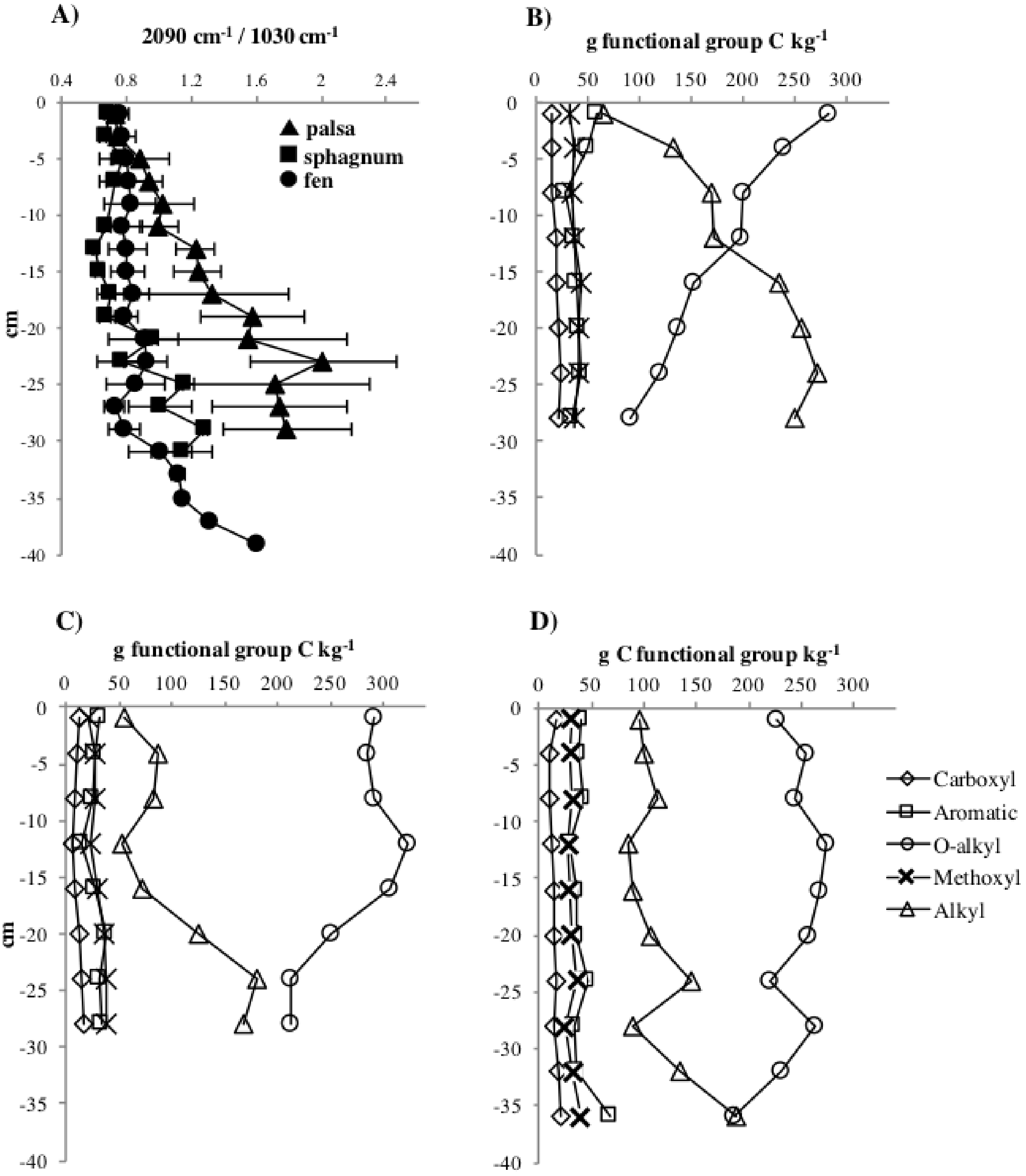

**Fig. 3. Soil profile C quality at the three vegetative communities. (A) FTIR humification ratio (2090 $cm^{-1}$/1030 $cm^{-1}$) for ▲ palsa, ■ sphagnum, and ● fen; (B) palsa distribution of $^{13}C$ NMR g functional group C $kg^{-1}$; (C) sphagnum distribution of $^{13}C$ NMR g functional group C $kg^{-1}$; (D) fen distribution of $^{13}C$ NMR g functional group C $kg^{-1}$.**

the woody shrub species (Nierop et al., 2001). In soil, increases in alkyl C may be representative of two processes: persistence and resistance of plant compounds with alkyl C functional groups (leaf cutins and root suberins) or the result of microbial transformation of labile species and accumulated by-products (Baldock et al., 1997; Clemente et al., 2013). The switch of functional group dominance from O-alkyl C to alkyl C at depth in palsa soil is likely due to production of microbial by-products from aerobic decomposition combined with preferential protection of alkyl C in small or hydrophobic soil particle regions (Simpson and Johnson, 2006; Lattao et al., 2008). Increases in total N and $\delta^{15}N$ with depth, comparable with NMR functional group changes, also reflected persistent organic compounds or selective decomposition. As decomposition continues both organic C and N are converted into inorganic forms, resulting in accumulation of non-labile residue in the soil (Reddy and DeLaune, 2008). The C/N ratio of the selectively preserved SOM has a lower C/N ratio (10–15) than fresh SOM (De la Rosa et al., 2008).

Sphagnum and fen soil profiles along the transect suggest changing vegetation communities and hydraulic conditions through time. Differences of SOM chemical composition in the lower depths of the sphagnum and fen soils could be attributed to former aerobic conditions where palsa vegetation thrived (Johansson et al., 2006). Peat developed in inundated conditions

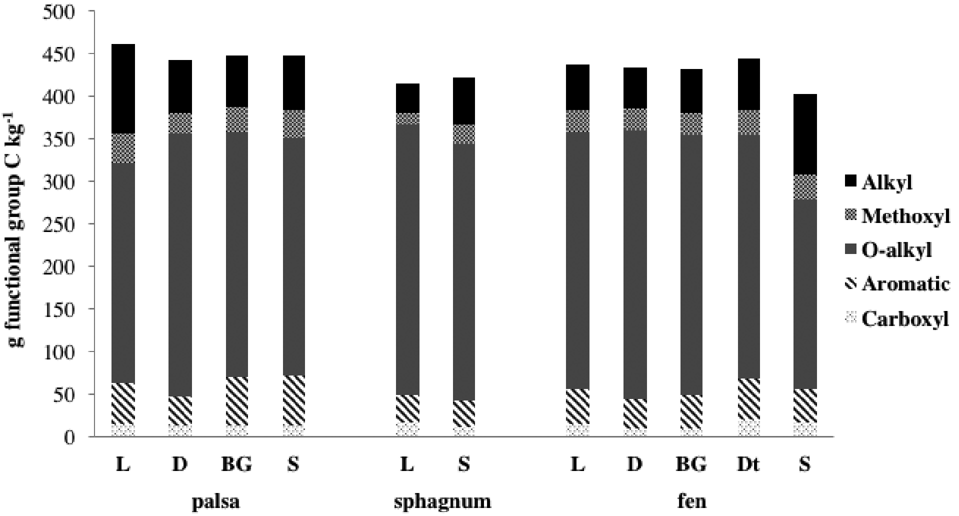

Fig. 4. The quantity of g functional group C $kg^{-1}$ as determined by $^{13}$C NMR along the decay continuum of the vegetation communities. L - live, D - dead, BG - below ground, Dt - detritus, S - 0-2 cm soil.

generally have stable organic matter signatures throughout the soil profile with little change in C composition or nutrient signatures (Krüger et al., 2014). Inundated sphagnum and fen sites initially had analogous content of labile SOM composition to comparative northern peatlands (Grover and Baldock, 2012; Tfaily et al., 2014). High O-alkyl C in sphagnum and fen vegetation inputs and surface soils originates from carbohydrate compounds which may rapidly deplete O-alkyl C under aerobic conditions favorable for decomposition (Leifeld et al., 2012). Dominance of O-alkyl C persisted in sphagnum and fen SOM until change points the soil profiles. The increased alkyl C below 15 cm in sphagnum soil and 25 cm in fen soil represented highly decomposed soil. The $\delta^{15}$N profiles of sphagnum and fen soils were initially depleted then steadily enriched to values similar to palsa soil. From 6 to 28 cm of the fen soil profile, C/N ratios and $\delta^{15}$N were similar to 0 to 20 cm of the sphagnum profile possibly indicating past ombrotrophic sphagnum vegetation and conditions at the site. However, the shift at depth to more enriched values suggests past aerobic conditions (Krüger et al., 2014). Soil organic matter chemical composition of deep sphagnum and fen soil may be indicative of legacy peat developed during palsa vegetative community presence and aerobic environmental conditions (Malmer et al., 2005). Highly decomposed signatures would likely not form under persistent anaerobic conditions in the current sphagnum and fen communities (Krüger et al., 2014). Past environmental regimes such as aerobic conditions could have promoted the extent of decomposition and subsequent accumulation of recalcitrant C as observed at deeper depths in the sphagnum and fen soil (Malmer et al., 2005; Routh et al., 2014).

## Total Nitrogen as an Indicator for Carbon Functional Groups

Decomposition changes N content in SOM due to loss of C to mineralization and immobilization of N by decomposers to approach C/N ratios similar to the decomposers (Wang et al., 2014; Krüger et al., 2014). Microbial biomass rapidly increases then complexes with existing organic matter resulting in non-cellular accumulation of N associated with SOM (Reddy and DeLaune, 2008). Therefore, C/N ratios of SOM have been related to the extent of decomposition. Similar to Borgmark and Schoning (2006), Tfaily et al., (2014) found a positive correlation of C/N ratio to lignin residue/carbohydrates, $r = 0.68$ and $n = 188$. In this study, $^{13}$C ssNMR analysis proved superior to FTIR as our results showed a stronger relationship of C quality to N storage. Leifeld et al. (2012) and Bonanomi et al. (2013) also determined that NMR functional groups were a better indicator of SOM processes. The percentage of O-alkyl C functional group (60–90 ppm) was the best proxy for aerobic peat soil respiration rates with 94% of variability explained compared with soil depth, C/N, O/C, H/C ratios, soil pH, and other C functional groups (Leifeld et al., 2012). In respect to litter decomposition, a ratio of specific O-alkyl signal (70–75 ppm) to methoxyl/N-alkyl C (52–57 ppm) best corresponded to litter decay rate ($r = 0.67$, $p > 0.01$; Bonanomi et al., 2013). With FTIR analysis, Pengerud et al. (2013) found cumulative mineralization of palsa mound, bog hummock, and fen lawn was positively correlated with a polysaccharide index (1185–915 $\text{cm}^{-1}$/SOC) and negatively correlated with a hydrophobicity

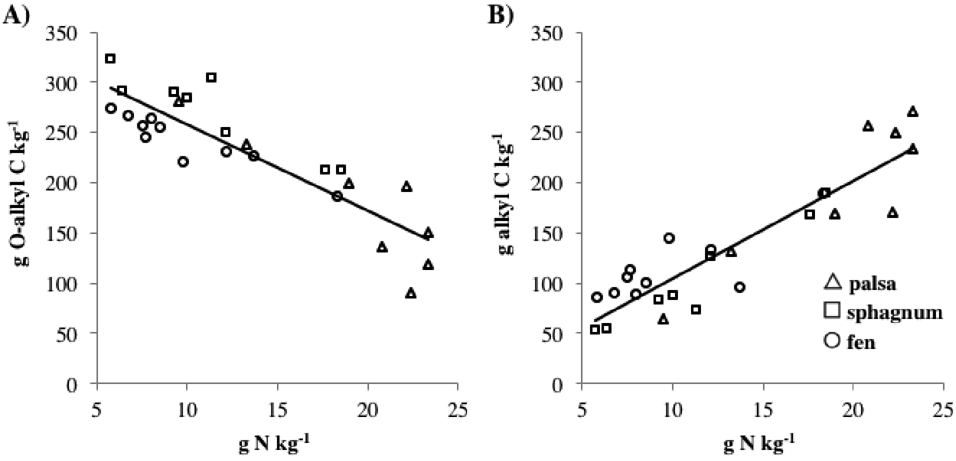

Fig. 5. (A) O-alkyl C ($r = –0.78$, $p < 0.001$, $n = 26$) and (B) alkyl C ($r = 0.83$, $p < 0.001$, $n = 26$) $^{13}$C NMR g functional group C $kg^{-1}$ plotted against g N $kg^{-1}$ with vegetative community distinguished by △ palsa, □ sphagnum, and ○ fen.

index (2985–2820 cm$^{-1}$/SOC). Therefore, ssNMR functional group C/N ratios may be a better indicator and predictor of decomposition than basic properties such as elemental ratios.

## CONCLUSIONS

Due to current permafrost thaw, palsa communities at Stordalen are increasingly collapsing potentially resulting in higher $CH_4$ production (De Jong et al., 2010). Bäckstrand et al. (2010) measured GHG emissions from the palsa communities at Stordalen which showed high $CO_2$ flux but minimal $CH_4$ flux. In contrast, $CH_4$ is emitted from sphagnum and fen communities with the fen communities producing over half of $CH_4$ emissions (Bäckstrand et al., 2008). Under favorable anaerobic conditions for methanogenesis, $CH_4$ emissions may increase at sites where fen communities have recently established in former sphagnum and palsa communities (Hodgkins et al., 2014). While areal and ground surveys document the surficial changes in vegetative communities, soil profiles give an indication of past environmental conditions using techniques such as colorimetric spectroscopy, macrofossils, biomarkers, and isotopes (De Jong et al., 2010). The SOM chemical composition from this study highlighted the inputs of varied vegetation communities in the past, thus capturing a history of organic matter inputs related to changes in wetland biogeomorphology.

The SOM chemical composition of palsa communities have implications on the current GHG emissions at Stordalen. Labile organic matter and high water table typically result in elevated $CH_4$ production (Whiting and Chanton, 2001). However, Hodgkins et al. (2014) showed that collapsed palsa at Stordalen did not produce $CH_4$ under anaerobic conditions. The minimal $CH_4$ emissions under anaerobic conditions may be due to the slowly degradable OM (high alkyl C and low O-alkyl C) in the palsa soils developed during aerobic conditions. Anaerobic production of $CO_2$ and $CH_4$ showed an inverse relationship with aliphatic SOM detected at wavelengths 2850 and 2920 cm$^{-1}$ from FTIR analysis (Hodgkins et al., 2014). Therefore, alkyl C may be an indicator for reduced anaerobic mineralization potential. Based on the strong correlations of key ssNMR C functional groups to total N, an increase in N in soil profiles may be a strong predictor of past organic C decomposition and depressed GHG production at peatlands like Stordalen when advanced SOM quality analyses (FTIR and $^{13}$C ssNMR) are not available. Future surveys of SOM biogeochemical parameters and C chemical composition should be pursued to better understand key processes affecting soil transformation and GHG emissions in peatland systems undergoing progressive changes in vegetation communities due to altered hydrology. Further analysis of more transects from Stordalen or other peatlands in the area would also be important to further validate these results.

## ACKNOWLEDGEMENTS

This study was supported in part by the NSF GRFP under Grant No. DGE-1315138 and NSF GROW travel award. NMR spectra were collected in the National High Magnetic Field Laboratory's AMRIS Facility which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida. Special thanks to Swedish hosts and field guides (Carmody McCalley, Anders Lindroth, and Torben Christensen), Dr. Kathy Curtis (UF-Soil and Water Sciences Mass Spec Laboratory) for stable isotope analysis, and Malak Tfaily (FSU Chemistry Department) for access to FTIR analysis.

## REFERENCES

Andersson, R.A., P. Meyers, E. Hornibrook, P. Kuhry, and C.M. Mörth. 2012. Elemental and isotopic carbon and nitrogen records of organic matter accumulation in a Holocene permafrost peat sequence in the East European Russian Arctic. J. Quaternary Sci. 27:545–552. doi:10.1002/jqs.2541

Bäckstrand, K., P.M. Crill, M. Mastepanov, T.R. Christensen, and D. Bastviken. 2008. Total hydrocarbon flux dynamics at a subarctic mire in northern Sweden. J. Geophys. Res. Biogeosci. 113(G3). doi:10.1029/2008JG000703

Bäckstrand, K., P.M. Crill, M. Jackowicz-Korezynski, M. Mastepanov, T.R. Christensen, and D. Bastviken. 2010. Annual carbon gas budget for a subarctic peatland, Northern Sweden. Biogeosciences 7:95–108. doi:10.5194/bg-7-95-2010

Baker, M.J., J. Trevisan, P. Bassan, R. Bhargava, H.J. Butler, K.M. Dorling, and F.L. Martin. 2014. Using Fourier transform IR spectroscopy to analyze biological materials. Nat. Protoc. 9:1771–1791. doi:10.1038/nprot.2014.110

Baldock, J.A., J.M. Oades, P.N. Nelson, T.M. Skene, A. Golchin, and P. Clarke. 1997. Assessing the extent of decomposition of natural organic materials using solid-state $^{13}$C NMR spectroscopy. Aust. J. Soil Res. 35:1061–1084. doi:10.1071/S97004

Bauer, I.E. 2004. Modelling effects of litter quality and environment on peat accumulation over different time-scales. J. Ecol. 92:661–674. doi:10.1111/j.0022-0477.2004.00905.x

Bliss, L.C., O.W. Heal, and J.J. Moore. 1981. Tundra ecosystems: A comparative analysis. Cambridge University Press, Cambridge.

Bonanomi, G., G. Incerti, F. Giannino, A. Mingo, V. Lanzotti, and S. Mazzoleni. 2013. Litter quality assessed by solid state $^{13}$C NMR spectroscopy predicts decay rate better than C/N and Lignin/N ratios. Soil Biol. Biochem. 56:40–48. doi:10.1016/j.soilbio.2012.03.003

Borgmark, A., and K. Schoning. 2006. 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

Breeuwer, A., M.M. Heijmans, B.J. Robroek, and F. Berendse. 2008. The effect of temperature on growth and competition between Sphagnum species. Oecologia 156:155–167. doi:10.1007/s00442-008-0963-8

Bridgham, S.D., J.P. Megonigal, J.K. Keller, B.B. Norman, and C. Trettin. 2006. The carbon balance of North American wetlands. Wetlands 26:889–916. doi:10.1672/0277-5212(2006)26[889:TCBONA]2.0.CO;2

Ciais, P., C. Sabine, G. Bala, L. Bopp, V. Brovkin, J. Canadell, A. Chhabra, R. DeFries, J. Galloway, M. Heimann, C. Jones, C. Le Quéré, R.B. Myneni, S. Piao, and P. Thornton. 2013. Carbon and other biogeochemical cycles In: T.F. Stocker et al., editors, Climate change 2013: The physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK. p. 465–570.

Clemente, J.S., M.J. Simpson, A.J. Simpson, S.F. Yanni, and J.K. Whalen. 2013. Comparison of soil organic matter composition after incubation with maize leaves, roots, and stems. Geoderma 192:86–96. doi:10.1016/j.geoderma.2012.08.007

De Jong, R., M. Blaauw, F.M. Chambers, T.R. Christensen, F. De Vleeschouwer, W. Finsinger, S. Fronzek, M. Johansson, U. Kokfelt, M. Lamentowicz, and G. Le Roux. 2010. Climate and peatlands. Springer Netherlands 85-121. doi:10.1007/978-90-481-8716-4_5

De la Rosa, J.M., H. Knicker, E. Lopez-Capel, D.A.C. Manning, J.A. Gonzalez-Perez, and F.J. Gonzalez-Vila. 2008. Direct detection of black carbon in soils by Py-GC/MS, carbon-13 NMR spectroscopy and thermogravimetric techniques. Soil Sci. Soc. Am. J. 72:258–267. doi:10.2136/sssaj2007.0031

Derenne, S., and T.T. Nguyen. 2014. Characterizing the molecular structure of organic matter from natural environments: An analytical challenge. C. R. Geosci. 346:53–63. doi:10.1016/j.crte.2014.02.005

Dixon, W.T., J. Schaefer, M.D. Sefcik, E.O. Stejskal, and R.A. McKay. 1982. Total suppression of spinning sidebands in CPMAS C-13 NMR. J. Magn.

Reson. 49:341–345.

Feng, X., A.J. Simpson, K.P. Wilson, D.D. Williams, and M.J. Simpson. 2008. Increased cuticular carbon sequestration and lignin oxidation in response to soil warming. Nat. Geosci. 1:836–839. doi:10.1038/ngeo361

Fenner, N., C. Freeman, M.A. Lock, H. Harmens, B. Reynolds, and T. Sparks. 2007. Interactions between elevated $CO_2$ and warming could amplify DOC exports from peatland catchments. Environ. Sci. Technol. 41:3146–3152. doi:10.1021/es061765v

Flanagan, L.B. 2013. Interacting controls on ecosystem photosynthesis and respiration in contrasting peatland ecosystems. In: D.T. Hanson and S.K. Rice, editors, Photosynthesis in bryophytes and early land plants. Springer, The Netherlands, p. 253–267. doi:10.1007/978-94-007-6988-5_14

Freeman, C., N. Ostle, N. Fenner, and H. Kang. 2004. A regulatory role for phenol oxidase during decomposition in peatlands. Soil Biol. Biochem. 36:1663–1667. doi:10.1016/j.soilbio.2004.07.012

Frolking, S., N.T. Roulet, E. Tuittila, J.L. Bubier, A. Quillet, J. Talbot, and P.J.H. Richard. 2010. A new model of Holocene peatland net primary production, decomposition, water balance, and peat accumulation. Earth Syst. Dynam. 1:115–167. doi:10.5194/esdd-1-115-2010

Frolking, S., J. Talbot, M.C. Jones, C.C. Treat, J.B. Kaukman, E. Tuittila, and N. Roulet. 2011. Peatlands in the Earth's 21st century climate system. Environ. Rev. 19:371–396. doi:10.1139/a11-014

Gorham, E. 1991. Northern peatlands: Role in the carbon cycle and probably responses to climatic warming. Ecol. Appl. 1:182–195. doi:10.2307/1941811

Grover, S.P.P., and J.A. Baldock. 2012. Carbon chemistry and mineralization of peat soils from the Australian Alps. Eur. J. Soil Sci. 63:129–140. doi:10.1111/j.1365-2389.2011.01424.x

Hodgkins, S.B., M.M. Tfaily, C.K. McCalley, T.A. Logan, P.M. Crill, S.R. Saleska, and J.P. Chanton. 2014. Changes in peat chemistry associated with permafrost thaw increase greenhouse gas production. Proc. Natl. Acad. Sci. USA 111:5819–5824. doi:10.1073/pnas.1314641111

Johansson, T., N. Malmer, P.M. Crill, T. Friborg, J.H. Aakerman, M. Mastepanov, and T.R. Christensen. 2006. Decadal vegetation changes in a northern peatland, greenhouse gas fluxes and net radiative forcing. Glob. Change Biol. 12:2352–2369. doi:10.1111/j.1365-2486.2006.01267.x

Knicker, H. 2011. Solid state CPMAS $^{13}C$ and $^{15}N$ NMR spectroscopy in organic geochemistry and how spin dynamics can either aggravate or improve spectra interpretation. Org. Geochem. 42:867–890. doi:10.1016/j.orggeochem.2011.06.019

Kokfelt, U., N. Reuss, E. Struyf, M. Sonesson, M. Rundgren, G. Skog, and D. Hammarlund. 2010. Wetland development, permafrost history and nutrient cycling inferred from late Holocene peat and lake sediment records in subarctic Sweden. J. Paleolimnol. 44:327–342. doi:10.1007/s10933-010-9406-8

Krüger, J.P., J. Leifeld, and C. Alewell. 2014. Degradation changes stable carbon isotope depth profiles in palsa peatlands. Biogeosciences 11:3369–3380. doi:10.5194/bg-11-3369-2014

Lafleur, P.M., T.R. Moore, N.T. Roulet, and S. Frolking. 2005. Ecosystem respiration in a cool temperate bog depends on peat temperature but not water table. Ecosystems 8:619–629. doi:10.1007/s10021-003-0131-2

Laiho, R. 2006. 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

Lamentowicz, M., Z. Balwierz, J. Forysiak, M. Płóciennik, P. Kittel, M. Kloss, and J. Pawlyta. 2009. Multiproxy study of anthropogenic and climatic changes in the last two millennia from a small mire in central Poland. Hydrobiologia 631(1):213–230. doi:10.1007/s10750-009-9812-y

Lattao, C., J. Birdwell, J.J. Wang, and R.L. Cook. 2008. Studying organic matter molecular assemblage within a whole organic soil by nuclear magnetic resonance. J. Environ. Qual. 37:1501–1509. doi:10.2134/jeq2007.0137

Leifeld, J., M. Steffens, and A. Galego-Sala. 2012. Sensitivity of peatland carbon loss to organic matter quality. Geophys. Res. Lett. 39. doi:10.1029/2012GL051856

Limpens, J., F. Berendse, C. Blodau, J. Canadell, C. Freeman, J. Holden, N. Roulet, H. Rydin, and G. Schaepman-Strub. 2008. Peatlands and the carbon cycle: from local processes to global implications – a synthesis. Biogeosciences 5:1475–1491. doi:10.5194/bg-5-1475-2008

Malmer, N., T. Johansson, M. Olsrud, and T.R. Christensen. 2005. Vegetation, climatic changes and net carbon sequestration in a North-Scandinavian subarctic mire over 30 years. Glob. Change Biol. 11:1895–1909.

Marin-Spiotta, E., N.T. Chaopricha, A.F. Plante, A.F. Diefendorf, C.W. Mueller, A.S. Grandy, and J.A. Mason. 2014. Long-term stabilization of deep soil carbon by fire and burial during early Holocene climate change. Nat. Geosci. 7:428–432. doi:10.1038/ngeo2169

Nierop, K.G., B. van Lagen, and P. Buurman. 2001. Composition of plant tissues and soil organic matter in the first stages of a vegetation succession. Geoderma 100:1–24. doi:10.1016/S0016-7061(00)00078-1

Nilsson, M., and M. Öquist. 2009. Partitioning litter mass loss into carbon dioxide and methane in peatland ecosystems. In: A.J. Baird et al., editors, Carbon cycling in Northern Peatlands. AGU, Washington, DC. p. 131–144. doi:10.1029/2008GM000819

Page, S.E., J.O. Rielley, and C.J. Banks. 2011. Global and regional importance of the tropical peatland carbon pool. Glob. Change Biol. 17:798–818. doi:10.1111/j.1365-2486.2010.02279.x

Pengerud, A., L. Cécillon, L.K. Johnsen, D.P. Rasse, and L.T. Strand. 2013. Permafrost distribution drives soil organic matter stability in a subarctic palsa peatland. Ecosystems 16:934–947. doi:10.1007/s10021-013-9652-5

Price, J.S., and G.S. Whitehead. 2004. The influence of past and present hydrological conditions on Sphagnum recolonization and succession in a block-cut bog, Québec. Hydrol. Processes 18:315–328. doi:10.1002/hyp.1377

Reddy, K.R., and R.D. DeLaune. 2008. Biogeochemistry of wetlands: Science and applications. CRC Press, Boca Raton, FL. doi:10.1201/9780203491454

Reddy, K.R., M.W. Clark, R.D. DeLaune, and M. Kongchum. 2013. Physicochemical characterization of wetland soils. In: R.D. DeLaune et al., editors, Methods in biogeochemistry of wetlands. Soil Science Society of America, Madison, Wisconsin. p. 41–53. doi:10.2136/sssabookser10.c3

Routh, J., G. Hugelius, P. Kuhry, T. Filley, P.K. Tillman, M. Becher, and P. Crill. 2014. Multi-proxy study of soil organic matter dynamics in permafrost peat deposits reveal vulnerability to climate change in the European Russian Arctic. Chem. Geol. 368:104–117. doi:10.1016/j.chemgeo.2013.12.022

Simpson, M.J., and P.C. Johnson. 2006. Identification of mobile aliphatic sorptive domains in soil humin by solid-state $^{13}C$ nuclear magnetic resonance. Environ. Toxicol. Chem. 25:52–57. doi:10.1897/05-152R.1

Simpson, A.J., D.J. McNally, and M.J. Simpson. 2011. NMR spectroscopy in environmental research: From molecular interactions to global processes. Prog. Nucl. Magn. Reson. Spectrosc. 58:97–175. doi:10.1016/j.pnmrs.2010.09.001

Talbot, J., P.J.H. Richard, N.T. Roulet, and R.K. Booth. 2010. Assessing long-term hydrological and ecological responses to drainage in a raised bog using paleoecology and a hydrosequence. J. Veg. Sci. 21:143–156. doi:10.1111/j.1654-1103.2009.01128.x

Tuomenvirta, H., A. Drebs, E. Forland, O.E. Tveito, E.V. Laursen, T. Jónsson, and J. Gama. 2013. nordklimdata1: Dataset for climate analysis with data from the Nordic region. R package version 1.0, http://CRAN.R-project.org/package=nordklimdata1.

Tfaily, M.M., W.T. Cooper, J.E. Kostka, P.R. Chanton, C.W. Schadt, P.J. Hanson, M.I. Colleen, and J.P. Chanton. 2014. Organic matter transformation in the peat column at Marcell Experimental Forest: Humification and vertical stratification. J. Geophys. Res. Biogeosci. 119:661–675. doi:10.1002/2013JG002492

Treat, C.C., W.M. Wollheim, R.K. Varner, A.S. Grandy, J. Talbot, and S. Frolking. 2014. Temperature and peat type control $CO_2$ and $CH_4$ production in Alaskan permafrost peats. Glob. Change Biol. 20:2674–2686. doi:10.1111/gcb.12572

Wang, M., T.R. Moore, J. Talbot, and P.J. Richard. 2014. The cascade of C:N:P stoichiometry in an ombrotrophic peatland: from plants to peat. Environ. Res. Lett. 9:024003. doi:10.1088/1748-9326/9/2/024003

Whiting, G.J., and J.P. Chanton. 2001. Greenhouse carbon balance of wetlands: methane emission versus carbon sequestration. Tellus B Chem. Phys. Meterol. 53:521–528. doi:10.1034/j.1600-0889.2001.530501.x

Wright, E.L., C.R. Black, A.W. Cheesman, T. Drage, D. Large, B.L. Turner, and S. Sjoegersten. 2011. Contribution of subsurface peat to $CO_2$ and $CH_4$ fluxes in a neotropical peatland. Glob. Change Biol. 17:2867–2881. doi:10.1111/j.1365-2486.2011.02448.x