



Long-term carbon and nitrogen dynamics at SPRUCE revealed through stable isotopes in peat profiles

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Abstract. Peatlands encode information about past vegetation dynamics, climate, and microbial processes. Here, we used $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ patterns from 16 peat profiles to deduce how the biogeochemistry of the Marcell S1 forested bog in northern Minnesota responded to environmental and vegetation change over the past $\sim 10\,000$ years. In multiple regression analyses, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ correlated strongly with depth, plot location, C / N, %N, and each other. Correlations with %N, %C, C / N, and the other isotope accounted for 80 % of variance for $\delta^{15}\text{N}$ and 38 % of variance for $\delta^{13}\text{C}$, reflecting N and C losses. In contrast, correlations with depth and topography (hummock or hollow) reflected peatland successional history and climate. Higher $\delta^{15}\text{N}$ in plots closer to uplands may reflect upland-derived DON inputs and accompanying shifts in N dynamics in the lagged drainage area surrounding the bog. The Suess effect (declining $\delta^{13}\text{C}$ since the Industrial Revolution) lowered $\delta^{13}\text{C}$ in recent surficial samples. High $\delta^{15}\text{N}$ from -35 to -55 cm probably indicated the depth of ectomycorrhizal activity after tree colonization of the peatland over the last 400 years, as confirmed by the occasional presence of wood down to -35 cm depth. High $\delta^{13}\text{C}$ at ~ 4000 years BP (-65 to -105 cm) could reflect a transition at that time to slower rates of peat accumulation, when ^{13}C discrimination during peat decomposi-

tion may increase in importance. Low $\delta^{13}\text{C}$ and high $\delta^{15}\text{N}$ at -213 and -225 cm (~ 8500 years BP) corresponded to a warm period during a sedge-dominated rich fen stage. The above processes appear to be the primary drivers of the observed isotopic patterns, whereas there was no clear evidence for methane dynamics influencing $\delta^{13}\text{C}$ patterns.

1 Introduction

Carbon (C) and nitrogen (N) cycling are tightly linked (Schlesinger et al., 2011) and understanding the controls of C and N turnover in boreal peatlands is fundamental to predicting whether this ecosystem will continue to function as a strong C sink or switch to a source of carbon dioxide (CO_2) and methane (CH_4) in response to environmental change. While 80–90 % of C deposited in peatlands is lost via decomposition and microbial respiration in the upper aerobic layers of the acrotelm (Belyea and Malmer, 2004), the deeper anaerobic catotelm accumulates recalcitrant *Sphagnum* litter and other organic matter due to low mineral nutrient availability and waterlogged conditions. Carbon loss from the catotelm can be 50 % within the first 1700 years with only an addi-

tional 15 % over the next 5800 years (Loisel et al., 2014), thus making peatlands an important long-term C sink.

Factors influencing C and N dynamics can be investigated using stable isotope measurements because biochemical and physical reactions proceed faster with lighter isotopes (^{12}C and ^{14}N) than with heavier isotopes (^{13}C and ^{15}N). Thus, different pools and fluxes can vary in their isotopic signatures (expressed as $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$). Climate and foliar %N can also influence the $\delta^{13}\text{C}$ of plant photosynthate by determining the relative rates of stomatal flux versus fixation of CO_2 (Brooks et al., 1998; Ménot and Burns, 2001; Sparks and Ehleringer, 1997). Radiocarbon measurements (^{14}C) are also important in biogeochemical research, as they allow dating of peat profiles and linking stable isotope patterns to specific climatic periods or vegetational phases of peatland succession. The dominant factors influencing organic C and N turnover can be identified by characterizing isotopic signatures of specific compounds or plant components through the peat profile (Nichols et al., 2009; Gavazov et al., 2016), but interpreting bulk peat signatures remains challenging. Deeper peats in the catotelm reflect both historic vegetation and accumulated effects of anaerobic fermentation occurring over thousands of years. In contrast, aerobic decomposition in the acrotelm alters biogeochemistry over shorter timescales.

Analysis of C and N in peatland cores is a potential way to determine key biogeochemical processes involved in organic matter burial and release. Cores taken through the peat profile trace the trajectory of peatland succession and contain the biogeochemical fingerprint of shifts in climate and vegetation states. For example, fens and bogs differ in the chemical and isotopic composition of the organic peat profile, reflecting differences in their pH, redox state, hydrologic inputs, and relative abundance of vascular plants compared to *Sphagnum* (Vitt and Weider, 2006). Warming, drying, and increased N availability can also alter isotopic composition through changes in plant community composition, with concomitant effects on C and N dynamics, including enhanced production of greenhouse gases such as CO_2 , CH_4 , and nitrous oxide (N_2O) (Yavitt et al., 1987; Regina et al., 1996; Bergman et al., 1999; Juutinen et al., 2010).

Our conceptual model of C and N dynamics during peatland succession is shown in Fig. 1. Methanogenesis, methanotrophy, refixation of methane-derived CO_2 , and plant composition influence the $\delta^{13}\text{C}$ of surficial layers (Ficken et al., 1998; Pancost et al., 2000), and the resulting $\delta^{13}\text{C}$ signal is subsequently altered further during diagenesis of these buried peat soils over time. Topography could also influence $\delta^{13}\text{C}$ because oxygen availability decreases with increasing water depth, resulting in different levels of methanogenesis and methanotrophy in hummocks versus hollows. Topography further influences $\delta^{13}\text{C}$ because hummock C is older than hollow C for equivalent depths below the mean bog surface. The anthropogenic addition of ^{13}C -depleted CO_2 to the atmosphere via the burning of fossil fuels (the

Suess effect; Ehleringer et al., 2000) also increases the gradient between ^{13}C -depleted surficial horizons and older, ^{13}C -enriched deeper horizons.

How N dynamics will influence $\delta^{15}\text{N}$ patterns is also shown in Fig. 1. In aerobic soils, uptake by mycorrhizal fungi and subsequent transfer of ^{15}N -depleted N to host plants increases the ^{15}N divergence between deeper, ^{15}N -enriched horizons and surficial horizons (Hobbie and Ouimette, 2009), with such processes presumably not operating in *Sphagnum* and deep-rooted nonmycorrhizal plants (Kohzu et al., 2003), but potentially operating in forested bogs. Nitrogen transport from uplands can be considerable in the lag drainage region surrounding a peatland (Verry and Janssens, 2011), and depending on the drainage $\delta^{15}\text{N}$, may influence the $\delta^{15}\text{N}$ of the receiving peatland. For example, lag drainage could contribute ^{15}N -depleted nitrate or ^{15}N -enriched dissolved organic N (DON) (Kalbitz and Geyer, 2002) that differ isotopically from N fixation (0 ‰) or atmospheric N inputs (Stewart et al., 1995; Högberg, 1997). In addition, biogeochemical hotspots are important for N dynamics in peatlands (Hill et al., 2016). Microbial processing of organic matter in soils commonly increases the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of the residual material (Nadelhoffer and Fry, 1994), although a N loss mechanism must also be present for $\delta^{15}\text{N}$ to be affected. Such processing decreases the C/N of organic matter, since respiratory C losses are generally greater than N losses.

Here, we used $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, %N, and %C patterns of peat profiles, plant tissues, and fungal hyphae sampled from the Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCe) experimental site in northern Minnesota, USA, at the Marcell S1 bog to investigate potential factors influencing C and N turnover in peatlands. In addition to the continuous variables of elemental concentration, isotopic signatures, and depth, nominal variables included plot location, topography (hummock versus hollow), and vegetation (near trees or not). We used concurrent radiocarbon measurements (Iversen et al., 2014) to link the stable isotope measurements to the 11 000-year history of C and N dynamics at the SPRUCe experimental site. With this combination of data, we studied how in situ biogeochemistry and peatland succession may have influenced the isotopic profiles. We inferred the path of peatland succession from a prior study of the nearby S2 bog, as given in Table 1. Successional history at S1 should be similar, with the vegetation proceeding from a rich fen to a transitional fen ~ 5500 years BP, transitioning to a poor fen ~ 2900 years BP, and then changing to a forested bog ~ 400 years BP.

Isotopic patterns reflect numerous biogeochemical processes. Here, we addressed four potential drivers of isotopic variation in a boreal peatland profile:

1. microbial processing and biochemical composition (as inferred from %N, %C, and C/N) will influence peatland $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$;

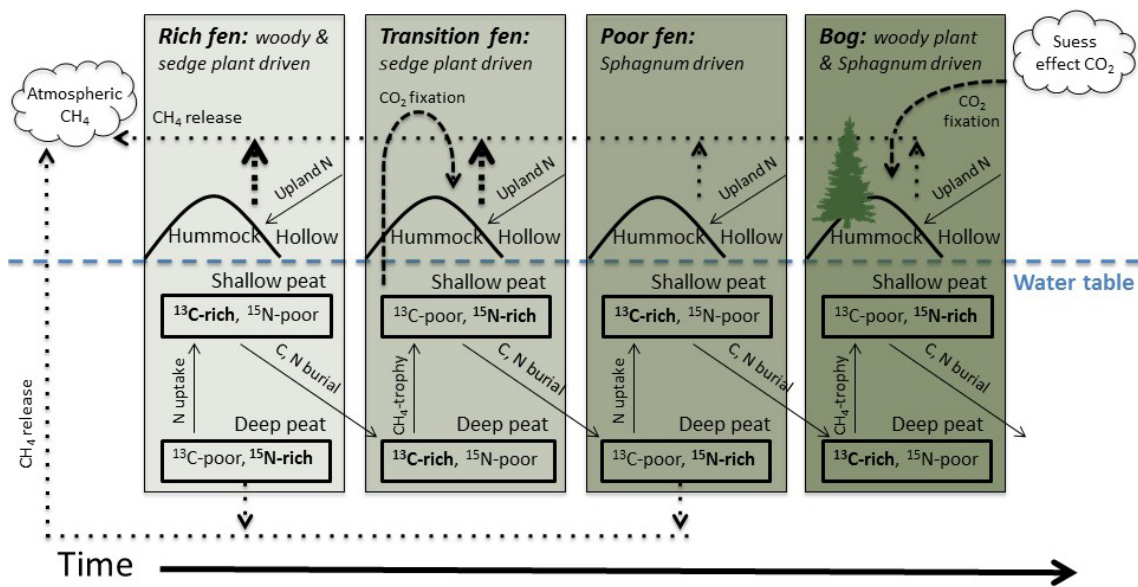


Figure 1. Conceptual diagram of movement of carbon (C) and nitrogen (N) during peatland development from rich fen to bog. Major processes influencing isotopic composition include methane (CH₄) flux from surficial and deeper layers (dotted upward arrow), methanotrophy and subsequent CO₂ recapture by *Sphagnum*, vascular plant transport of methane, N uptake by vascular plants and mycorrhizal fungi, and the sequestration of C and N over time in deeper peat. Assimilation of ¹³C-depleted CO₂ from the Suess effect influences modern peat carbon (rightmost top box); N flux from adjacent uplands influences productivity in the lagg region, peatland topography of hummocks and hollows influences methanogenesis and methanotrophy, and trees influence partitioning of nitrogen. Climate (not shown) will influence the initial δ¹³C of fixed carbon. By rotating the figure 90° counterclockwise, the lower boxes correspond stratigraphically to the peat profile.

Table 1. Peatland stages at SPRUCE based on stratigraphy at the S2 watershed in the Marcell National Forest, USA (Verry and Janssens, 2011). MAT: mean annual temperature; MAP: mean annual precipitation.

Stage	Years BP	Climate
Rich fen-sedge peat	9300–7400	MAT 4–5 (°C), MAP 700 mm
	9200–6500	Warm and dry
	8400–5500	
	7400–6100	4 °C → 2 °C, MAP 700–800 mm
	6500–6000	Cooling trend
Transitional fen	6100–3200	Stable climate
	5600–3000	
Open poor fen	3200–2400	Cooled slightly
	2900–390	
Little Ice Age	2000–1800	Warmer and drier
	600–150	Cooled 1 °C, MAT 800 mm
Forested bog	384/130–now	

- proximity to uplands will increase N concentrations and peat δ¹⁵N;
 - peatland colonization by ectomycorrhizal trees will increase peat δ¹⁵N and the ¹⁵N enrichment between surficial and deeper peat.
 - in upper peat layers, ¹³C depletion will reflect anthropogenic declines in the δ¹³C of atmospheric CO₂ (Suess effect).
- In addition to these drivers, we will examine the covariation of peat δ¹³C and δ¹⁵N with climate or vegetation through the Holocene.

2 Methods

2.1 Site description

Soil and fungal samples were collected from the SPRUCE experimental site at the 8 ha S1 bog in the USDA Forest Service Marcell Experimental Forest in northern Minnesota, USA (47°30.476' N, 93°27.162' W). The bog is dominated by the trees *Picea mariana* (Mill.) Britton, Sterns and Poggenb. and *Larix laricina* (Du Roi) K. Koch; ericaceous shrubs (*Ledum groenlandicum* Oeder; *Chamaedaphne calyculata* (L.) Moench.); and *Sphagnum* mosses. Various forbs and sedges are also present. The bog topography can be separated into hummocks (protruding above the average water table) and depressed hollows, and divided into areas with trees (*Picea* or *Larix*) or without trees. Average annual air temperature from 1961 to 2005 was 3.3 °C with yearly mean extremes of −38 and 30 °C and average annual precipitation of 768 mm (Sebestyen et al., 2011). Average pH of the peat is 4.1 and average gravimetric water content is 7.40 g H₂O g^{−1} dry peat (Iversen et al., 2014). The water table fluctuates about 30 cm annually and water table depth can reach 1.4 m over the course of a 50-year record (Sebestyen et al., 2011). The bog maintains a perched water table with a hydraulic gradient about 1 m above the surrounding aquifer, which is composed of outwash sand (Verry et al., 2011). Because of the high water table, root distribution is quite shallow compared to upland sites (Iversen et al., 2017). In total, 93 % of fine roots were in the 0–10 cm depth, 6 % at 10–20 cm depth, and only 1 % at 20–30 cm depth (A. Malhotra, personal communication, 2017). The boundary between the acrotelm and catotelm at SPRUCE is around 30–40 cm depth.

2.2 Procedures

Peat cores for this analysis were collected in mid-August of 2012 from locations along three boardwalks extending out into the bog beyond the lagg region (Fig. 2). Surface peat (~0–30 cm) was collected using a modified hole saw, while deeper samples down to mineral soil (~30–250 cm) were collected using a Russian peat corer. Cores were taken in both hummocks and hollows, with 0 cm defined as the surface of hollows and hummock heights above that assigned positive depths. Cores were bulked and homogenized every 10 cm over the 0 to −100 cm depth, every 25 cm from −100 to −200 cm, and over the entire 50 cm increment from −200 to −250 cm (in some cases, −300 cm was reached before mineral soil was observed). Cores were sampled at 17 locations (Fig. 2; the locations of experimental plots distributed across the three boardwalks) and material from 16 of these locations was used for the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and radiocarbon measurements reported here. At locations 4, 5, 6, and 7 along the southern boardwalk, separate cores were taken within 150 cm of *Picea* or *Larix* trees and in the open (no trees

within 150 cm), and the distinction designated as “treed” or “untreed”.

Peat cores were analyzed for $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, %C, %N, and C/N by depth increment, with the depth increment recorded as the average depth (for example, 0 to 10 cm in a hummock given as 5 cm). Peat cores were analyzed in hummocks to a depth of −10 cm and in hollows to the bottom of the core (between −200 and −300 cm). Live woody plant foliage and fine roots to −10 cm were collected in August 2012 and live *Sphagnum* in 2013.

To collect fungal hyphae, in-growth cores were constructed. Mesh (40 μm) in-growth bags (10 cm \times 10 cm) were filled with sterile sand. Bags were incubated in the field in paired hummock and hollows at six locations in the bog. In hummocks, bags were inserted at +10 to 0 cm above the adjacent hollow and in both locations from 0 to −10 cm and −10 to −20 cm below the hollow surface. Bags were installed on 5 June 2013 and recovered on 20 September 2013. Sand from in-growth bags was combined with ultrapure water and mixed at 80 rpm for 20 min. Suspended hyphae were removed with tweezers and the process was repeated until all hyphae were collected. Hyphal biomass was dried in the oven at 60 °C for 48 h. Of 30 in-growth samples, 20 generated enough hyphal mass for analysis. All 20 samples were treated as independent replicates in statistical analyses.

2.3 Isotopic and elemental analysis

Radiocarbon content of homogenized bulk peat was measured on the Van de Graaff FN accelerator mass spectrometer (AMS) at the Center for AMS at Lawrence Livermore National Laboratory. Peat samples were not chemically pretreated prior to ^{14}C measurement. Samples were prepared by sealed-tube combustion to CO₂ in the presence of CuO and Ag and then reduced onto Fe powder in the presence of H₂ (Vogel et al., 1984). Radiocarbon isotopic values had an average AMS precision of 2.6‰ and were corrected for mass-dependent fractionation with $\delta^{13}\text{C}$ values from analyses conducted at the Department of Geological Sciences Stable Isotope Laboratory at the University of California, Davis, using a GVI Optima stable isotope ratio mass spectrometer. Radiocarbon values are reported here in $\Delta^{14}\text{C}$ notation corrected for ^{14}C decay since 1950 (Stuiver and Polach, 1977). Calibrated ages were determined using Calib (<http://calib.qub.ac.uk/calib/>) or CaliBomb (Reimer et al., 2004) with INTCAL13 (Reimer et al., 2013) and Northern Hemisphere Zone 1 bomb curve extension (Hua et al., 2013) atmospheric ^{14}C calibration curves. Years before present (BP) refer to years prior to 1950. For more recent samples, calendar years AD may also be used.

These same soil samples and additional samples of hyphae and foliage were analyzed for %C, %N, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ at the University of New Hampshire Stable Isotope Laboratory using a Costech 4010 elemental analyzer coupled to a Thermo Delta Plus XP IRMS. Standard deviations of labora-

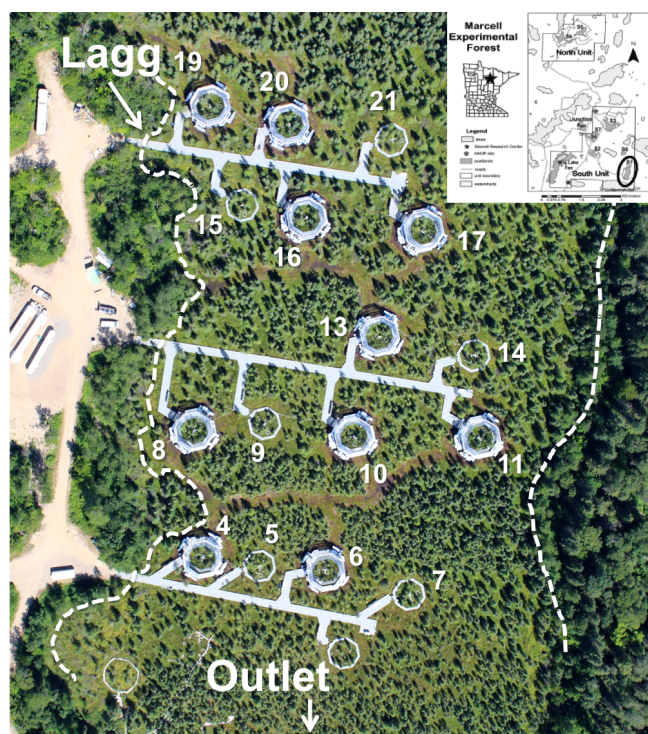


Figure 2. Aerial photograph of the S1 bog showing the 16 experimental plots (each 10.4 m in diameter to the outer edge of the visible perimeter boardwalk). Plot numbers on the image represent the plot areas within which peat was sampled. The lag boundary is delineated with a dashed line, and the inset indicates the location of the bog within Minnesota and the Marcell Experimental Forest.

tory standards (tuna, NIST 1515, and NIST 1575a) for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ averaged less than 0.2‰. Fine roots of the woody vascular plants were analyzed for their stable isotopic composition at the Oak Ridge National Laboratory on an Integra CN mass spectrometer (SerCon, Crewe, UK), using standards traceable to NIST 8547-ammonium sulfate or 8542-sucrose (NIST, Gaithersburg, Maryland, USA).

2.4 Statistical tests

The statistical program JMP (SAS Institute, Middleton, Massachusetts, USA) was used for statistical analyses. Reported values are \pm SE, unless otherwise specified. Regression models for soil $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were tested. Factors included in the regression model included nominal variables of vegetation type (treed or non-treed), topography (hollow or hummock), and plot number. Depths with only a single measurement were generally excluded, unless they were very similar in depth to another value. Continuous variables included %N, %C, and isotopic values.

To test whether plot location, proximity to trees, depth, topography, and elemental concentrations influenced the carbon and N isotope patterns in peat profiles, we used multiple regression analyses. Sample %C, %N, C / N, and either $\delta^{13}\text{C}$

or $\delta^{15}\text{N}$ were included as continuous variables. Because the effects of depth or plot location on N and C dynamics are unlikely to change continuously (for example, methanogenesis requires an anaerobic soil and plots at bog edges may have different hydrology and N dynamics than plots in the middle of the bog; Urban and Eisenreich, 1988), plot was treated as a nominal (categorical) variable in our regression models. To avoid over-parameterizing the model, depth was treated as a continuous variable with a cubic transformation (that is, the regression model included model depth, the square of model depth, and the cube of model depth as additional parameters). Stepwise regression was used and model selection based on the lowest Akaike information criterion with a correction for sample size (AICc). Within a given depth, values for radio-carbon were tested for correlations against $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and the slope of the regression estimated.

3 Results

3.1 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in plants and fungal hyphae

Of the six vascular plant taxa tested, $\delta^{13}\text{C}$ of foliage varied from -30‰ in *Larix* to -28‰ in *Picea*. The $\delta^{15}\text{N}$ of plant foliage varied more widely than $\delta^{13}\text{C}$, from -8.5‰ for *Picea* to 2.5‰ for *Eriophorum*. Fine root $\delta^{13}\text{C}$ averaged $-27.4 \pm 0.3\text{‰}$ for *Larix*, $-26.9 \pm 0.1\text{‰}$ for *Picea*, and $-28.5 \pm 0.2\text{‰}$ for shrubs. Fine root $\delta^{15}\text{N}$ averaged $-4.7 \pm 0.4\text{‰}$ for *Larix*, $-4.1 \pm 0.3\text{‰}$ for *Picea*, and $-1.8 \pm 0.1\text{‰}$ for shrubs, whereas coarse roots of shrubs averaged $-3.4 \pm 0.3\text{‰}$. If we assume plant productivity patterns are similar aboveground and belowground, then the productivity-weighted average in vascular plants for $\delta^{13}\text{C}$ was -29.2‰ for foliage and -27.3‰ for roots (Table 2). Fungal hyphae from in-growth cores ($n = 20$) averaged $-26.0 \pm 0.2\text{‰}$ (se) for $\delta^{13}\text{C}$ and $-0.3 \pm 0.2\text{‰}$ for $\delta^{15}\text{N}$.

3.2 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in peat profiles

Carbon isotope ($\delta^{13}\text{C}$) values of peat in the profile increased from -29‰ in the top 10 cm of hummocks and hollows to -26‰ at -112 cm and then decreased slightly at greater depths. $\delta^{13}\text{C}$ values changed most rapidly from 0 cm to -50 cm depth (Fig. 3a). Nitrogen isotope values in the peat profile increased from -3‰ in hummocks above the water level to around 1‰ at -50 cm . $\delta^{15}\text{N}$ then decreased to 0‰ at -85 cm before increasing again to 1.5‰ at -200 cm . Similar to $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ changed most rapidly from 0 cm to -50 cm depth (Fig. 3b).

In a stepwise regression model for $\delta^{13}\text{C}$ including $\delta^{15}\text{N}$, C / N, %N, %C, and depth as continuous variables and the vegetation type, topography, and plot sampling location as nominal variables, all factors were retained in our final model, including four terms for partitioning the 16 plots. The model explained 85 % of the total variance ($n = 238$, adjusted r^2) in peat $\delta^{13}\text{C}$. The three depth terms (depth, depth

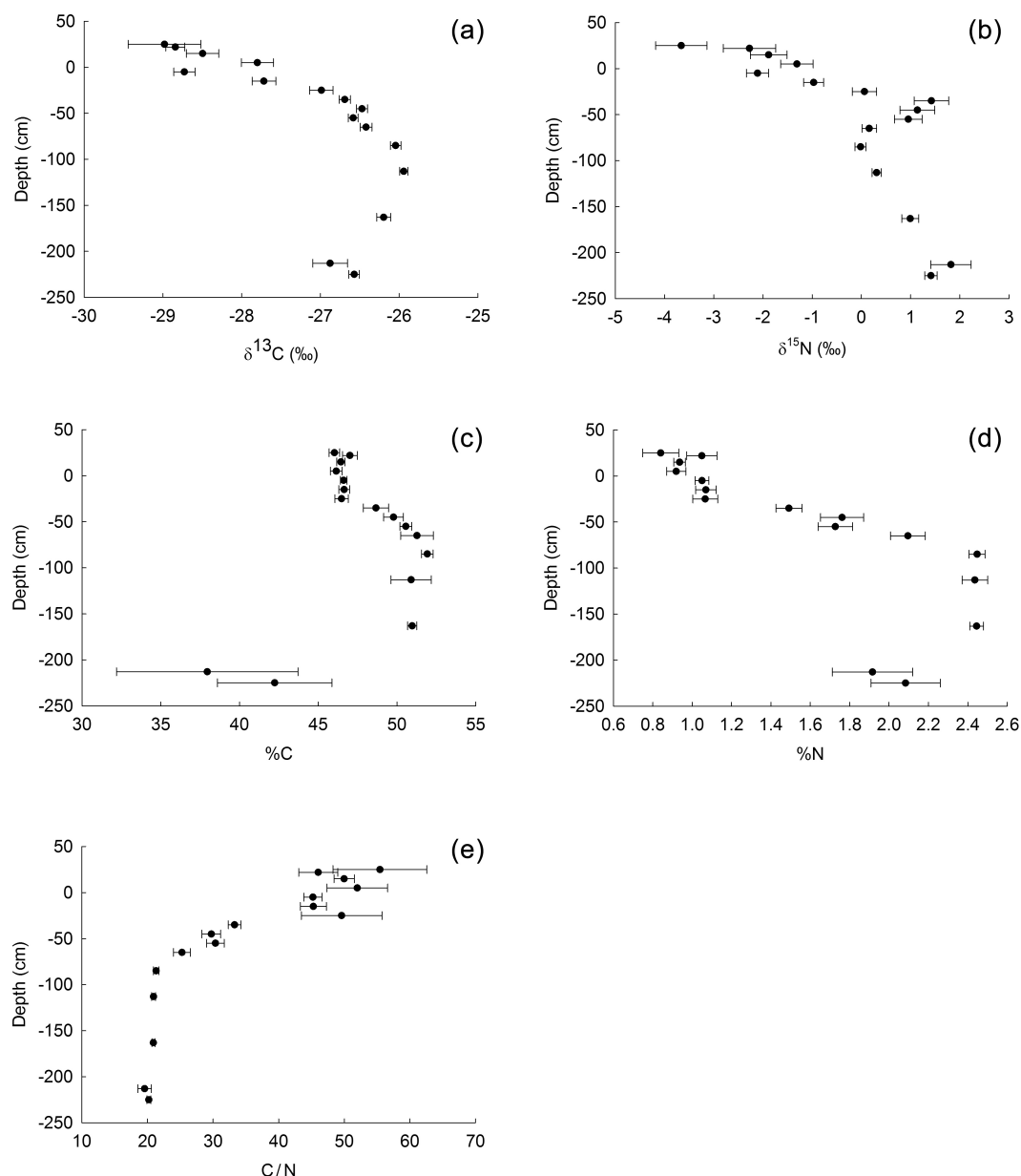


Figure 3. $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, %N, %C, and C / N versus depth. Values ($\pm\text{SE}$) are averaged across hummock versus hollow cores and across treed versus non-treed cores. Averages ($\pm\text{SE}$) are given for each depth, with n given in parentheses following the depth: 25 (3), 22 (7), 15 (14), 5 (14), -5 (19), -15 (17), -25 (17), -35 (15), -45 (17), -55 (17), -65 (17), -85 (18), -112 (17), -162 (17), -213 (3), and -225 cm (8). (a) $\delta^{13}\text{C}$ versus depth, (b) $\delta^{15}\text{N}$ versus depth, (c) %C versus depth, (d) %N versus depth, and (e) C / N.

squared, and depth cubed) explained 45 %, %N explained 10 %, C / N 11 %, $\delta^{15}\text{N}$ 15 %, %C explained 2 %, the four plot terms explained 7 %, and proximity to trees explained 3 % of the variance (Table 3). Topography explained 10 % of variance, with hollows lower than hummocks by 0.89‰ in $\delta^{13}\text{C}$ ($p < 0.001$). Results of the stepwise model testing $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are given in Table S1.

The stepwise regression model for $\delta^{15}\text{N}$ of peat included $\delta^{13}\text{C}$ and the same variables as in the $\delta^{13}\text{C}$ regression model. This model explained 66 % of the total variance (adjusted

r^2), with proximity to trees and topography dropping out of the regression model. Of the explained variance, the three depth terms accounted for 8 %, %N 22 %, %C 7 %, C / N 17 %, $\delta^{13}\text{C}$ 34 %, and the three plot terms 11 % (Table 3).

The influence of depth and location in our regression models on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values is plotted in Figs. 4 and 5, respectively. The influence of depth was negative above 0 cm (corresponding to the surface of the hollows), increased regularly from -5 to -25 cm, and then varied little in $\delta^{13}\text{C}$ in the deepest horizons while still increasing in $\delta^{15}\text{N}$. There was

Table 2. Average foliar values for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, %C, %N, and C/N ($n = 7$).

Species	$\delta^{13}\text{C} \pm \text{SE}$	$\delta^{15}\text{N} \pm \text{SE}$	%C $\pm \text{SE}$	%N $\pm \text{SE}$	C/N $\pm \text{SE}$	n	%C flux ¹
<i>Chamaedaphne</i>	-29.5 ± 0.1^c	-3.8 ± 0.4^c	51.30 ± 0.42^a	1.50 ± 0.04^b	34.53 ± 0.88^{cd}	12	1.5
<i>Eriophorum</i>	-28.4 ± 0.2^a	2.5 ± 0.6^a	45.16 ± 0.21^c	1.45 ± 0.06^b	31.49 ± 1.36^d	9	–
<i>Larix</i>	-30.4 ± 0.1^d	-6.3 ± 0.4^d	48.49 ± 0.36^{bc}	0.77 ± 0.06^c	65.10 ± 5.17^b	7	37
<i>Ledum</i>	-29.2 ± 0.1^{bc}	-5.4 ± 0.2^d	51.74 ± 0.23^a	1.26 ± 0.03^b	41.21 ± 1.07^c	13	6.6
<i>Picea</i>	-28.0 ± 0.2^a	-8.5 ± 0.2^e	49.07 ± 0.20^b	0.63 ± 0.02^c	79.44 ± 3.24^a	11	38.3
<i>Smilacina</i>	-28.7 ± 0.2^{ab}	0.1 ± 0.3^b	47.20 ± 0.53^d	2.46 ± 0.10^a	19.53 ± 0.88^e	12	1.5
<i>Sphagnum</i> ²	-29.2	-2	–	–	–	–	15
Hollow ³	-28.8 ± 0.1	-2.3 ± 0.2					
Hummock ³	-28.8 ± 0.1	-2.3 ± 0.5					

¹ Weighted average of $\delta^{13}\text{C}$ inputs is -29.2‰ , based on carbon fixation measurements of different taxa (R.J. Norby, personal communication). ANOVA comparing means in vascular plants used a post hoc Tukey test, with log C/N tested in place of C/N. ² Data from Tfaily et al. (2014). ³ Top 10 cm only, primarily *Sphagnum*. Different superscripted letters after numbers within a column indicate a significant ($p < 0.05$) Tukey post hoc ANOVA test.

Table 3. Stepwise regression model for explaining $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in peat profiles at SPRUCE. Plot, topography (hummock versus hollow), and nearby presence of trees are treated as nominal variables. Value = Coefficient $\pm \text{SE}$; Var = % variance explained; $n = 238$. Depth in cm, depth-squared and depth-cubed terms are also included in the model. Plots are sequentially separated into two groups to maximize the variance explained. Plot groups are Group 1, {19 & 8 & 11 & 20 & 10 & 15 & 5 vs. 9 & 16 & 21 & 6 & 14 & 4 & 7 & 13 & 17}; Group 2, {15 vs. 5}; Group 3, {9 & 16 & 921 & 6 & 14 & 4 & 7 vs. 13 & 17}; Group 4, {14 & 4 vs. 7}; Group 5, {10 & 6 & 11 & 13 & 9 & 15 vs. 17 & 16 & 5 & 8 & 14 & 20 & 7 & 21 & 19 & 4}; Group 6, {13 vs. 9}; Group 7, {17 & 16 & 5 & 8 & 14 & 20 & 7 & 21 vs. 19 & 4}. Within a group, the first plots listed have the given value, the second plots listed (after vs.) have the negative of the given value.

$\delta^{13}\text{C}$ model, adjusted $r^2 = 0.846$, $p < 0.001$				$\delta^{15}\text{N}$ model, adjusted $r^2 = 0.660$, $p < 0.001$			
Source	Value $\pm \text{SE}$	%Var	P	Source	Value $\pm \text{SE}$	%Var	P
Intercept	-28.39 ± 0.37	–	<0.001	Intercept	32.30 ± 3.39	–	<0.001
$\delta^{15}\text{N}$	0.196 ± 0.025	14.8	<0.001	$\delta^{13}\text{C}$	1.164 ± 0.115	34	<0.001
%N	1.036 ± 0.162	9.5	<0.001	%N	-2.963 ± 0.360	22.5	<0.001
%C	-0.033 ± 0.011	2.3	0.002	%C	0.107 ± 0.023	7	<0.001
C/N	0.025 ± 0.004	11	<0.001	C/N	-0.060 ± 0.008	17.1	<0.001
Hummock	0.44 ± 0.07	9.6	<0.001	Hummock	–	–	–
Treed	-0.12 ± 0.05	3.5	0.023	Treed	–	–	–
Depth	$-4.18 \pm 0.44\text{e}^{-2}$	21.2	<0.001	Depth	$-2.48 \pm 0.63\text{e}^{-2}$	5.1	<0.001
Depth ²	$-3.28 \pm 0.40\text{e}^{-4}$	15.4	<0.001	Depth ²	$-1.57 \pm 0.68\text{e}^{-4}$	1.8	0.021
Depth ³	$-7.03 \pm 1.21\text{e}^{-7}$	7.9	<0.001	Depth ³	$-4.89 \pm 2.27\text{e}^{-7}$	1.6	0.032
Group 1	-0.121 ± 0.031	3.5	<0.001	Group 5	-0.305 ± 0.070	6.3	<0.001
Group 2	0.151 ± 0.081	1.3	0.062	Group 6	0.280 ± 0.188	0.7	0.137
Group 3	-0.111 ± 0.047	1.5	0.018	Group 7	-0.308 ± 0.090	3.9	<0.001
Group 4	-0.163 ± 0.065	1.2	0.013				

some spatial patterning of values across plots, with two plots (4 and 19) near to the western upland high in $\delta^{15}\text{N}$ (Figs. 2 and 5).

Although overall patterns of radiocarbon with depth were clear, radiocarbon varied widely at any given depth, and correlated significantly with $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ at several depths (Table 4). Radiocarbon correlated positively with $\delta^{13}\text{C}$ at -162 , -5 , 5 , and 15 cm, and correlated negatively with $\delta^{13}\text{C}$ at -35 and -65 cm. In contrast, radiocarbon correlated positively with $\delta^{15}\text{N}$ at -65 , -55 , -45 , -5 , and 15 cm, and correlated negatively with $\delta^{15}\text{N}$ at -162 and -25 cm. Overall patterns

of $\Delta^{14}\text{C}$ with $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ are shown in Fig. 6a and b, respectively.

4 Discussion

4.1 Potential causes of shifts in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in peat profiles

Isotopic ratios within the profile can shift if elemental fluxes in or out of the system differ isotopically from profile material (Fig. 1). Loss of labile C via respiration, methanogenesis, or leaching (Kolka et al., 1999) could alter the $\delta^{13}\text{C}$ of the

Table 4. Correlations between radiocarbon and stable isotopes by depth, and mean $\Delta^{14}\text{C}$ for that depth. Hummock vs. hollow plots and treed vs. non-treed plots were averaged together. $\delta^{13}\text{C} \pm \text{SE}$ and $\delta^{15}\text{N} \pm \text{SE}$ columns reflect the shift in $\Delta^{14}\text{C}$ with a 1 ‰ shift in $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$. Statistically significant correlations are bolded.

Depth		Mean±SE	Age		$\delta^{13}\text{C} \pm \text{SE}$		$\delta^{15}\text{N} \pm \text{SE}$	
	<i>n</i>	$\Delta^{14}\text{C}$ (‰)	(cal yr BP)	adj. <i>r</i> ²	(‰)	<i>P</i>	(‰)	<i>P</i>
25	3	52 ± 5	Modern	0.881	10 ± 3	0.157	2 ± 9	0.892
22	7	29 ± 13	Modern	0.325	69 ± 35	0.106	2 ± 11	0.889
15	16	59 ± 5	Modern	0.219	13 ± 6	0.039	7 ± 3	0.038
5	16	115 ± 18	Modern	0.682	74 ± 13	<0.001	17 ± 14	0.225
−5	19	71 ± 7	Modern	0.352	33 ± 10	0.004	18 ± 6	0.01
−15	19	126 ± 19	Modern	−0.053	9 ± 30	0.762	−16 ± 22	0.459
−25	20	100 ± 23	Modern	0.018	−41 ± 35	0.261	−62 ± 16	0.001
−35	18	−102 ± 34	1580 ± 180	0.228	−246 ± 100	0.026	−9 ± 24	0.704
−45	18	−182 ± 27	1730 ± 260	−0.041	−54 ± 95	0.575	58 ± 12	<0.001
−55	18	−203 ± 19	nd	−0.025	−63 ± 81	0.447	52 ± 12	<0.001
−65	18	−288 ± 11	2800 ± 600	0.486	−100 ± 24	<0.001	44 ± 14	0.006
−85	18	−359 ± 7	3520 ± 90	−0.007	−23 ± 25	0.362	−7 ± 15	0.651
−113	18	−392 ± 6	3950 ± 90	0.081	42 ± 27	0.134	−17 ± 15	0.276
−163	17	−486 ± 7	6000 ± 500	0.713	68 ± 11	<0.001	−31 ± 7	<0.001
−213	3	−587 ± 32	9200 ± 200	−0.811	−44 ± 136	0.801	−11 ± 76	0.912
−225	11	−567 ± 12	6775 ± 260	−0.089	27 ± 62	0.677	9 ± 33	0.784

nd: not determined.

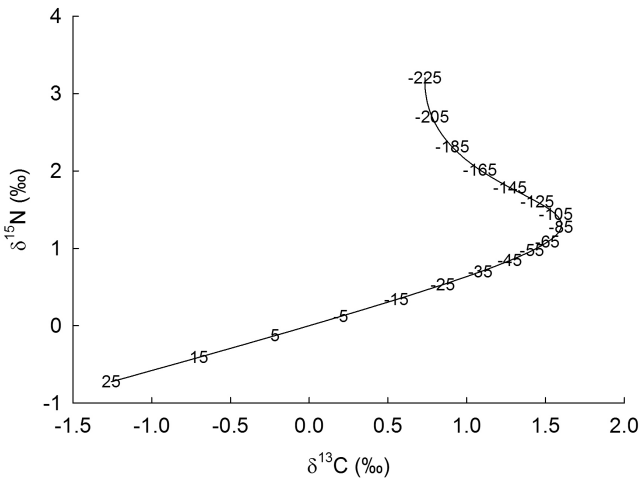


Figure 4. Depth coefficients of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ calculated from the three depth terms in the regression models. The depth in centimeters for specific points is indicated on the line.

residual material, as could inputs of ^{13}C -enriched material such as roots or mycorrhizal hyphae. Similarly, changes in the $\delta^{13}\text{C}$ of atmospheric CO_2 can alter the $\delta^{13}\text{C}$ of photosynthetically fixed C, whereas changes in moisture, temperature, or photosynthetic capacity can alter the ^{13}C discrimination between atmospheric CO_2 and fixed C. For N, loss of ^{15}N -depleted material from the bulk peat via mycorrhizal transfer to fine roots, direct root uptake, denitrification, or leaching of organic or inorganic N could raise the $\delta^{15}\text{N}$ of the remaining

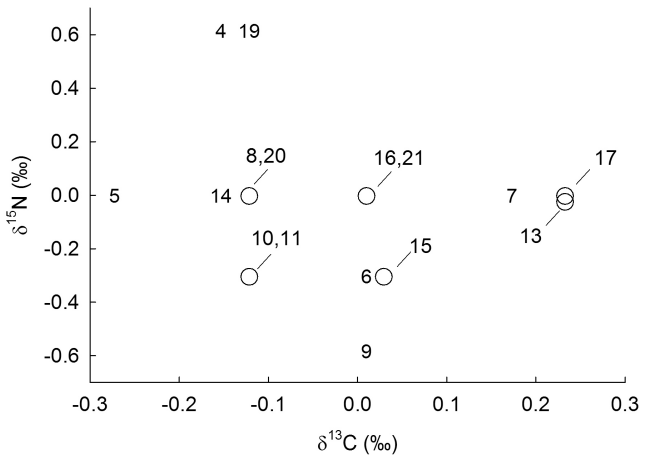


Figure 5. Plot coefficients of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ from regression models in peat profiles, as calculated from Table 1. The plot number is the symbol for the paired coefficient values. For clarity, plots with identical or near-identical values are indicated with circles.

soil organic matter. Inputs of N via atmospheric deposition, N fixation, or transport from surrounding uplands could also influence $\delta^{15}\text{N}$ if these inputs differ isotopically from peat profile values. These processes can be linked to past climate and vegetation with profile radiocarbon measurements that are calibrated to calendar years. Here, we used radiocarbon to indicate the potential timing of shifts in some of the primary drivers that influenced C and N stable isotope patterns within the peat profiles at SPRUCE, such as the Suess effect

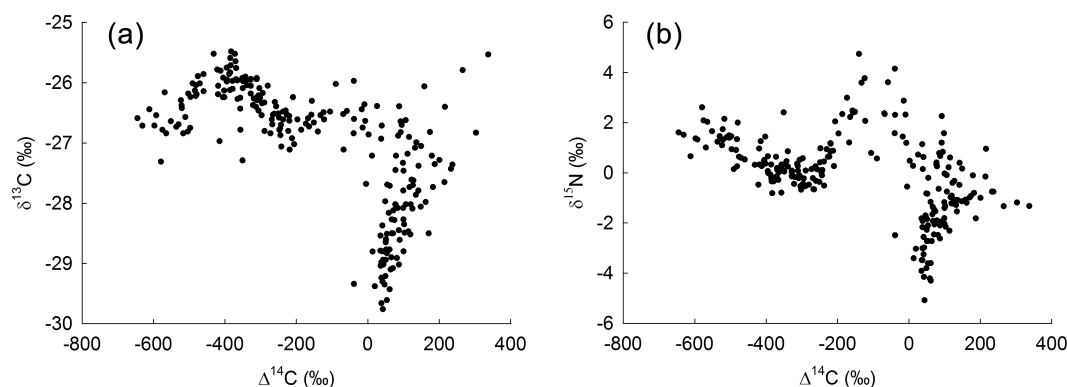


Figure 6. Relationship between $\Delta^{14}\text{C}$ and (a) $\delta^{13}\text{C}$; (b) $\delta^{15}\text{N}$.

and the transition to a forested bog, but also examined processes that were not tied to a particular time period, such as differences in C and N stoichiometry or proximity to uplands.

4.2 %N, %C, and C : N stoichiometry influenced $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ patterns

%N, %C, and C / N contributed a combined 47 and 23 % of explained variance, respectively, to our regression models of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$. These factors reflected the biochemical and isotopic composition of the original plant material, but also reflected how the chemical structure and isotopic composition of plant material has altered during its slow decomposition at S1.

Microbially driven C loss raises soil organic matter %N, lowers C / N, and enriches soil organic matter in ^{13}C (resulting from loss of ^{13}C -depleted CO_2) (Ehleringer et al., 2000; Alewell et al., 2011). The positive correlation of %N with $\delta^{13}\text{C}$ may therefore reflect an underlying correlation between the accumulation of ^{13}C -enriched microbial necromass (Wallander et al., 2004) and the increased N content of the peatland organic matter. Fungal %N and $\delta^{13}\text{C}$ are positively correlated (Hobbie et al., 2012) because of the high $\delta^{13}\text{C}$ of microbially synthesized protein relative to other microbial components such as carbohydrates and lipids. In contrast, the positive correlation of C / N with $\delta^{13}\text{C}$ and negative correlation with $\delta^{15}\text{N}$ presumably reflect a legacy of buried wood, which, relative to other plant material, should be high in $\delta^{13}\text{C}$ (Trudell et al., 2004) and high in C / N. This can be seen clearly in the few samples with C / N greater than 70, which is higher than any plant tissue measured in this study. Although some *Sphagnum* taxa under pristine conditions can be very low in %N (0.22 %) and $\delta^{15}\text{N}$ (-3.6‰) and high in C / N (~ 190) (Asada et al., 2005a), here, the presence of wood was noted seven times during laboratory examination of the 238 samples at depths from 15 to -35 cm , with those samples twice as high in C / N (average, 69) as other samples and also significantly higher in C / N in multiple regression analysis (see Table S2).

The negative correlation of %N with $\delta^{15}\text{N}$ indicated that either added or removed N is low in $\delta^{15}\text{N}$. One possibility for removal is that ^{15}N -depleted N has been transferred from mycorrhizal fungi to plants. Alternatively, N could be added via fixation with a $\delta^{15}\text{N}$ value of -1‰ , which would lower overall $\delta^{15}\text{N}$ values deeper in the peat profile. However, we point out that only at -45 and -55 cm are %N and $\delta^{15}\text{N}$ significantly and negatively correlated (Table S3). At these depths, %N is about 1.8 % and $\delta^{15}\text{N}$ is about 1‰ (Fig. 3b, d). The value of the coefficient for %N in the $\delta^{15}\text{N}$ regression, -2.96‰ \%N^{-1} , implied that the perturbing N has a $\delta^{15}\text{N}$ value that is $1.8\text{‰} \times 2.96\text{‰ \%N}^{-1}$ less than that of 1‰ , or -4.3‰ , which is too low to be fixed N. The apparent ^{15}N depletion of 5.3‰ against the source N is a plausible value for ^{15}N discrimination between mycorrhizal fungi and host plants (Hobbie and Colpaert, 2003).

Correlations of carbon concentration with stable isotopes provide information about chemical composition or degree of processing. The negative correlation of %C with $\delta^{13}\text{C}$ is expected based on the chemical composition of ^{13}C -depleted compound classes of lignin, aromatics, and lipids, which are high in %C (Poorter et al., 1997; Hobbie et al., 2002). Initial decomposition of *Sphagnum* commonly decreases $\delta^{13}\text{C}$, as ^{13}C -enriched soluble components are leached (Asada et al., 2005b). In contrast, aromatics and lipids do not generally contain N, so the positive correlation of %C with $\delta^{15}\text{N}$ in bulk peat cannot be explained in the same manner. However, microbial processing generally enriches soils in ^{15}N (Billings and Richter 2006; Templer et al., 2007) while increasing %C, which was also true at S1 (Tfaily et al., 2014).

4.3 Proximity to uplands and trees increased peat $\delta^{15}\text{N}$

Plot-specific coefficients for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ may reflect site-specific differences in the dominance of conditions favoring ^{13}C - or ^{15}N -depleted losses during peatland development. The positive coefficients for $\delta^{15}\text{N}$ are from two plots, 4 and 19, closest to the lagg region adjacent to the western upland. This suggests that the different hydrology in the lagg

has enhanced ^{15}N fractionation from N removal mechanisms such as denitrification, nitrification, or leaching of DON. Alternatively, dissolved N transported from the uplands during spring thaw and melt may have provided an additional ^{15}N -enriched N source for plots 4 and 19 located near the bog edges (Fig. 5). Peatland DON appears enriched in ^{15}N and ^{13}C relative to bulk peat (Broder et al., 2012), and this is presumably true for upland sources as well. In the adjacent Marcell S2 kettle bog, large N fluxes from upland locations from both surface runoff and interflow led to much larger N losses in streamflow from the lag region ($\sim 32 \text{ kg ha}^{-1} \text{ yr}^{-1}$) than from the bog itself ($2 \text{ kg ha}^{-1} \text{ yr}^{-1}$) (Urban and Eisenreich, 1988). The uplands here are dominated by ectomycorrhizal trees such as *Populus*, *Quercus*, and *Pinus*, which produce vertically stratified soil profiles with high $\delta^{15}\text{N}$ values in lower organic and mineral horizons (Hobbie and Ouimette, 2009). We therefore expect DON produced in uplands to be high in $\delta^{15}\text{N}$, which will serve as a source of ^{15}N -enriched N to lag regions of peatlands.

4.4 $\delta^{15}\text{N}$ patterns with depth reflected climate and vegetation

Peatland succession and climate have been established previously at the nearby S2 bog and are summarized in Table 1. As the same climatological factors affected the S2 and S1 (SPRUCE) bogs, plant stratigraphy and isotopic patterns were probably similar, although accumulation rates are lower at S1 than at S2 (McFarlane, unpublished data).

In the following paragraphs, we link shifts in $\delta^{15}\text{N}$ through the profile to radiocarbon ages and the corresponding patterns in vegetation and climate at the S2 bog. The high $\delta^{15}\text{N}$ at -213 and -225 cm corresponded approximately to a warm period between 8000 and 9200 years BP, during a sedge-rich fen stage (Verry and Janssens, 2011), with mean annual temperatures of $4\text{--}5^\circ\text{C}$. Given similar C/N ratios during this period to subsequent periods (~ 20), nitrogen losses were probably more depleted in ^{15}N than subsequent losses, that is, more losses via nitrate leaching or denitrification rather than via DON leaching. Nitrification and denitrification are higher in fens than in bogs and should change $\delta^{15}\text{N}$ patterns along the core profile as the core reflects peatland succession and climatological changes (Regina et al., 1996; Bayley et al., 2005; Wray and Bayley, 2007).

The S2 bog shifted from a rich fen to a transitional fen by 5600 years BP, while mean annual temperature (MAT) decreased to perhaps 2°C . At the S1 bog, the negative correlation between radiocarbon and $\delta^{15}\text{N}$ at -162 cm (~ 6000 years BP) suggested decreasing losses of ^{15}N -depleted N during this transition. The depth increment from -85 to -112 cm corresponded to a transitional fen stage 3300–4800 years BP. The accompanying trough in $\delta^{15}\text{N}$ at -400‰ $\Delta^{14}\text{C}$ (4220 calibrated years BP, Fig. 6b) suggested decreased sequestration of ^{15}N -enriched organic matter as nutrient availability declined during this transition.

The positive correlations between $\delta^{15}\text{N}$ and $\Delta^{14}\text{C}$ at -45 , -55 , and -65 cm (Table 4 and Fig. 6b) are linked to a parallel decline in ‰N over these time periods, so that younger samples are lower in ‰N and higher in $\delta^{15}\text{N}$ than older samples, reflecting losses of ^{15}N -depleted N from the younger samples. $\delta^{15}\text{N}$ values peaked at -35 to -55 cm, and then declined above and below those depths. This pattern suggested that those depths were affected by a ^{15}N enrichment process that did not affect deeper depths (that is, further in the past). The peak $\delta^{15}\text{N}$ accordingly reflected ^{15}N partitioning between surficial and deeper horizons by a new mechanism.

We suggest that ectomycorrhizal fungi are the most probable cause of this unusual peak in $\delta^{15}\text{N}$ at intermediate depths in the peat bog. At the nearby S2 bog, poor fen transitioned to forested bog between AD 1610 and 1864, with a charcoal layer at S2 indicating that peat was consumed by fire during this period, precluding a more specific date for this transition (Verry and Janssens, 2011). This forested bog is dominated by ectomycorrhizal *Picea* and *Larix*. Transfer to plants of ^{15}N -depleted N by ectomycorrhizal fungi leads to low plant $\delta^{15}\text{N}$ and high ^{15}N enrichment of the residual N not transferred (Hobbie and Hobbie, 2008; Hobbie and Höglberg, 2012). Here, the apparent influence of ectomycorrhizal uptake can be traced to ~ -55 cm.

The relatively low contribution of ectomycorrhizal and ericoid mycorrhizal fungi to total plant uptake here compared to forest sites dominated by ectomycorrhizal fungi accounted for the lower ^{15}N enrichment between surficial layers and deeper layers here ($\sim 3\text{‰}$) than in forest soils, which averaged a 9.6‰ enrichment between surficial and deeper soils for ectomycorrhizal forests (reviewed in Hobbie and Ouimette, 2009). Ectomycorrhizal and ericoid mycorrhizal trees and shrubs contributed relatively little to total N uptake at the nearby Marcell S2 bog, where mosses contributed 75 % of total plant uptake, herbaceous plants 13 %, and mycorrhizal trees and shrubs 13 % (Urban and Eisenreich, 1988). A few studies in peatlands have reported $\delta^{15}\text{N}$ values through profiles, but those values have peaked at -1 to 0‰ and have been in systems without ectomycorrhizal trees present (Krüger et al., 2015; Esmeijer-Liu et al., 2011).

4.5 $\delta^{13}\text{C}$ patterns with depth reflected climatic factors

Once shifts in $\delta^{13}\text{C}$ caused by compositional shifts are removed, the remaining patterns can be explained by invoking climatic or vegetation shifts. The relatively low $\delta^{13}\text{C}$ at -213 and -225 cm corresponded to a warm period between 8000 and 9200 years BP, during a sedge-dominated rich fen stage (Verry and Janssens, 2011), with mean annual temperatures of $4\text{--}5^\circ\text{C}$. Higher temperatures in peatlands are associated with lower $\delta^{13}\text{C}$ values (Skrzypek et al., 2005, 2008).

Radiocarbon and $\delta^{13}\text{C}$ correlated positively at -162 cm, corresponding to a 1‰ rise in $\delta^{13}\text{C}$ which accompanied a drop in MAT to perhaps 2°C by 6000 years BP. This cooling trend was also accompanied by a slight rise in precipitation,

so the decreased ^{13}C discrimination could also be attributed to increased *Sphagnum* moisture (Rice and Giles, 1996), although it is difficult to distinguish between these two possible causes of ^{13}C differences (Ménot and Burns, 2001). *Sphagnum* discrimination is less with increased moisture because CO_2 diffusion is limited under wet conditions. The stratigraphy at the S2 bog indicated a vegetational shift from a rich fen to a transitional fen during this period.

The depth increment from -85 to -112 cm corresponded to a transitional fen stage 3300–4800 years ago. In our regression model for $\delta^{13}\text{C}$ (Fig. 4), these two depths are about 0.5‰ higher in $\delta^{13}\text{C}$ than at -162 cm. The peak in $\delta^{13}\text{C}$ may reflect a phase during which sedges transported methane directly to the atmosphere, thereby minimizing the refixation in *Sphagnum* cells of ^{13}C -depleted, methanotrophic-derived carbon dioxide (Raghoebarsing et al., 2005).

4.6 The Suess effect increased ^{13}C depletion in surficial peat

The strong dependence of $\delta^{13}\text{C}$ on peat depth partially reflected the 1.7‰ decline in the $\delta^{13}\text{C}$ of atmospheric CO_2 since 1850, with the lowest $\delta^{13}\text{C}$ values above the water table, where C is of recent origin. For example, the lowest estimated values of the $\delta^{13}\text{C}$ depth coefficients ($\sim -1\text{‰}$) in hummocks at 15, 22, and 25 cm above the mean hollow surface reflect C from the last 50 years (Fig. 4), as confirmed by $\Delta^{14}\text{C}$ averages of 59, 29, and 52‰ for these three depths, where only C influenced by ^{14}C created during thermonuclear testing should have positive $\Delta^{14}\text{C}$ values (Table 4). Although our sampling lacked sufficient vertical resolution to explicitly include corrections for the Suess effect (e.g., as done in Esmeijer-Liu et al., 2012), the $\sim 2\text{‰}$ increase in the depth coefficient of our $\delta^{13}\text{C}$ regression model from the hummocks to deeper in the profile correspond well to the long-term shift in $\delta^{13}\text{C}$ of atmospheric CO_2 from preindustrial times to the present. An additional factor contributing to the higher depth coefficient could be the $1\text{--}2\text{‰}$ higher $\delta^{13}\text{C}$ in roots than in foliage and the different input depths of foliage (surface only) and roots (distributed throughout the acrotelm). The steady increase in $\delta^{13}\text{C}$ between -5 and -25 cm depth (Fig. 4) presumably reflected the increasing dominance of preindustrial C. Depths of -35 cm and below all had $\Delta^{14}\text{C}$ values less than -100‰ (Table 4), indicating primarily pre-bomb and preindustrial C when the average $\delta^{13}\text{C}$ of atmospheric CO_2 was -6.5‰ (versus the current value of -8.2‰). In addition, modern production of organic matter averaged -29‰ in $\delta^{13}\text{C}$ (Table 2), similar to values for surficial horizons, whereas deeper horizons were between -27 and -26‰ . The Suess effect of $\sim 1.5\text{‰}$ therefore accounted for at least half of this difference.

5 Conclusions

Although the multiple potential interactions among climate, vegetation, and soil processes made definitive conclusions difficult, we identified several factors that influenced $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ patterns in peatland profiles, including the Suess effect, C and N stoichiometry, microbial processing, proximity to uplands, and tree colonization. The potential roles of methanogenesis versus respiration in influencing $\delta^{13}\text{C}$ could not be addressed using bulk samples, since ^{13}C shifts were relatively small. Future measurements of deuterium isotope ratios (δD) would allow separation of effects of respiration (loss of CO_2) versus methane flux on $\delta^{13}\text{C}$ patterns, since methanogenesis discriminates against deuterium. Our conceptual model as given in Fig. 1 included the Suess effect (influencing $\delta^{13}\text{C}$ patterns) and N transport from uplands (probably influencing $\delta^{15}\text{N}$ patterns), but missed several additional factors that appeared to be important in controlling the isotopic patterns we reported. Buried wood appeared to influence both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ directly, and the ectomycorrhizal fungi associated with tree species here created a ^{15}N -enriched horizon that may be specific to forested peatlands. The model did not consider N loss mechanisms and associated ^{15}N effects, nor did it consider the potential for ^{13}C differences between roots and aboveground litter to influence $\delta^{13}\text{C}$ profiles. One potential way forward is to put these multiple processes into quantitative models of peatland development that includes vegetation succession and climatic drivers, such as the Holocene Peatland Model (Frolking et al., 2010), and to adapt these models to make isotopic predictions that can be compared against data. Such model–data comparisons should continue to improve our ability to interpret isotopic patterns, as well as reveal areas where our model formulations are currently inadequate.

Data availability. The data presented in this study are available in the appendices and through the Iversen et al. (2014) publication.

The Supplement related to this article is available online at doi:10.5194/bg-14-2481-2017-supplement.

Author contributions. Samples were collected by Colleen M. Iversen, Paul J. Hansen, and Kirsten S. Hofmockel and analyzed by Janet Chen, Erik A. Hobbie, Colleen M. Iversen, and Karis J. McFarlane. Erik A. Hobbie prepared the manuscript with contributions from all authors.

Competing interests. The authors declare that they have no conflict of interest.

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