

The Fate of ^{15}N Tracer in Waterlogged Peat Cores from Two Central European Bogs with Different N Pollution History

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Abstract Under low nitrogen (N) input into rain-fed peat bogs, *Sphagnum* moss efficiently filters incoming N, preventing invasion of vascular plants and peat oxygenation. Elevated atmospheric N deposition, in combination with climatic warming, may cause retreat of bryophytes and degradation of peat deposits. There are concerns that higher emissions of greenhouse gases, accompanying peat thinning, will accelerate global warming. Breakthrough of deposited N below living moss has been quantified for two Central European peat bogs dominated by *Sphagnum magellanicum*. In the 1990s, the northern site, ZL, received three times more atmospheric N ($> 40 \text{ kg ha}^{-1} \text{ year}^{-1}$) than the southern site, BS. Today, atmospheric N inputs at both

sites are comparable (15 and $11 \text{ kg ha}^{-1} \text{ year}^{-1}$, respectively). Replicated peat cores were collected from the wet central segments of both study sites, $^{15}\text{N-NO}_3^-$ tracer was applied on the moss surface, and the peat cores were incubated under water-logged conditions. After 40 weeks, the rate of downcore leaching of the ^{15}N tracer was assessed. The recent history of high N pollution at ZL did not accelerate ^{15}N penetration into deeper peat layers, relative to BS. At both sites, less than 3% of the ^{15}N tracer reached the shallow depth of 9 cm. Analysis of control peat cores, along with a ^{210}Pb chronology, revealed removal of the “excess” N from the ZL peat profiles prior to sampling. Following a decrease of atmospheric N pollution in the past two decades, efficient filtering of atmospheric N by *Sphagnum* at ZL has been renewed.

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1 Introduction

Since the beginning of the Industrial Revolution, anthropogenic emissions of reactive nitrogen (N_r), mainly nitrate (NO_3^-) and ammonium (NH_4^+), have more than doubled atmospheric N_r deposition (Galloway et al. 2004). Today, the biogeochemical cycle of N belongs to the most disturbed cycles among all chemical elements (Johnson and Lindberg 1992). Large amounts of ammonium originate from agricultural practices, whereas nitrate is primarily derived from industrial operations (Dise et al. 2011). Urbanization contributes to the

emissions of both reduced and oxidized forms of N_r (Gabor et al. 2017).

Wetlands represent a sizeable store of N, amounting approximately to 16% of global soil N (Wieder and Vitt 2006). There are concerns that global warming, in combination with elevated N deposition, will cause peat degradation and thinning (Gorham 1991, Granath et al. 2014). This will be accompanied by higher biogenic emissions of greenhouse gases (CO_2 , CH_4 , N_2O) which, in turn, may accelerate global warming (Clymo et al. 1998, Sheppard et al. 2013). While fertilization with elevated N inputs may lead to higher net primary productivity in rain-fed bogs, it will also augment microbial decomposition (Breeuwer et al. 2008, Song et al. 2017). It appears that accelerated litter decomposition under high N deposition is typical only of the early stages of peat formation. By contrast, high N deposition may slow down decomposition of recalcitrant organic matter in later stages of peat formation (Manninen et al. 2016).

Most high-latitude peatlands are severely N-limited (Sorrell et al. 2011). Lamers et al. (2000) interpreted the response of *Sphagnum* mosses to increasing N deposition as a three-step process with different underlying biogeochemical controls. Under low N depositions ($< 12 \text{ kg N ha}^{-1} \text{ year}^{-1}$), increasing N input has no effect on N concentrations in *Sphagnum*. Incoming N is rapidly taken up by the moss because N availability limits the growth. Nitrogen concentration is determined by productivity and not by N deposition rates. Increased C uptake leads to a relatively constant N concentration. Under medium N depositions ($12\text{--}18 \text{ kg N ha}^{-1} \text{ year}^{-1}$), there is a positive relationship; higher N inputs lead to higher N concentration in the moss. Nitrogen is no longer a growth-limiting nutrient and it accumulates in the tissue. Under high N depositions ($18\text{--}60 \text{ kg N ha}^{-1} \text{ year}^{-1}$), there is again no positive response. Atmospheric N inputs are no longer bound to the moss layer; the ecosystem reaches N saturation. Nitrogen is leached into deeper bog layers, where it becomes available to the roots of vascular plants. An invasion of vascular plants is detrimental to the preservation of C and N pools in wetland soil. The roots of vascular plants introduce oxygen to deeper peat layers and augment decomposition of organic matter (Heijmans et al. 2002). Litter of vascular plants per se is more easily degradable than litter of *Sphagnum*, also decreasing C and N accumulation (Jirousek et al. 2011). The scenario by Lamers et al. (2000) has been modified by Bragazza et al. (2005, 2006) and Harmens et al. (2014).

The mechanisms responsible for the mass transfer of atmospheric N into *Sphagnum* (the top ca. 5 cm) and peat (deeper than 5 cm) are still poorly understood (Xing et al. 2011). Downward translocation of atmospheric N could be dominated by particulate organic N (Blodau et al. 2006) or microbial immobilization following the transport of dissolved N_r along a concentration gradient (Pinsonneault et al. 2016).

In recent years, Lamers's threshold for N breakthrough and leaching (ca. $18 \text{ kg N ha}^{-1} \text{ year}^{-1}$) has been tested in several N polluted bogs (e.g., Xing et al. 2011, Chiwa et al. 2016, Zając and Blodau, 2016). These data have shown that under N-rich conditions (over $18 \text{ kg N ha}^{-1} \text{ year}^{-1}$) *Sphagnum* still can effectively filter inorganic N and immobilize it in the thin topmost layer.

Nitrogen has two stable isotopes, ^{14}N (natural abundance of 99.635%) and ^{15}N (natural abundance of 0.365%). The heavier stable isotope ^{15}N has been used as an efficient tracer of translocations and transformations of N in natural systems. An artificial mixture containing 98% of ^{15}N was applied in several field and laboratory studies to investigate the dispersion of atmospheric N in the wetland (Li and Vitt 1997; Franzes and Loiseau 1999; Williams et al. 1999, Nordbakken et al. 2003; Blodau et al. 2006; Xing et al. 2011; Fritz et al. 2014; Zając and Blodau, 2016). These studies typically combined high and low water table periods, relative to the capitula of living *Sphagnum*. As a rule, inclusion of a (natural or simulated) drought resulted in a higher downward mobility of atmospheric N in peat. The ^{15}N tracer reached the unsaturated *Sphagnum* and substrate surfaces above the low water table almost immediately following its application (Williams et al. 1999). Vice versa, water saturation resulted in slower penetration of the tracer into deeper substrate layers (Blodau et al. 2006). In the long term, such experimental designs gave realistic results on the overall vertical mobility of N in peat, but the maximum depth reached by the tracer often reflected the relative duration of high and low water table conditions; the longer the drought, the deeper the tracer distribution. In our previous studies (Novak et al. 1994, 2003, Vile et al. 2000, Bohdalkova et al. 2013), we observed that large segments of mountain-top ombrotrophic peat bogs in Central Europe (usually those situated close to a bog water pool) remained water-saturated throughout the year. Given that the hydraulic conductivity in saturated peat rapidly decreases with an increasing depth, the question arises of how the

generally wet conditions in Central European peat bogs affect the vertical N mobility in peat.

Here, we present a ^{15}N tracer study using replicated peat cores from two *Sphagnum*-dominated sites with contrasting N pollution histories. Until recently, the industrial northeast of the Czech Republic received three times more atmospheric N than the semi-natural ecosystems in the southwest (Fottova 2003). Today, both regions receive similar, relatively small amounts of atmospheric N. Our objective was to evaluate the robustness of N retention in waterlogged *Sphagnum* peat at a northeastern and a southwestern site by comparing the rates of penetrating of atmospheric N_r into deeper substrate layers. We hypothesized that at the northeastern site N saturation at a time of peak air pollution 20–30 years ago could have led to N leaching and removal from the peat profiles. Present-day N filtering capacity of living *Sphagnum* at the northeastern site could be re-established, becoming as high as the N filtering capacity at the southwestern site.

2 Materials and Methods

2.1 Study Sites

The two study sites are ombrotrophic, *Sphagnum*-dominated peat bogs situated in spruce forested mountains near the state borders of the Czech Republic, Central

Europe (Fig. 1, Table 1). Since the beginning of the Holocene (11.5 thousand years *BP*), both sites have accumulated at least 7 m of freshwater peat (Dohnal et al. 1965). The less polluted study site, Blatenska stat (BS), is part of the Sumava Mts. National Park in southwestern Bohemia. The area near BS is dominated by forestry and agriculture. Torfowisko Pod Zielencem (ZL) is located in Silesia, Poland, 260 km northeast of BS, 3 km from the Czech border. ZL and the nearby Eagle Mts. are situated in the vicinity of a highly industrialized area with numerous open-pit soft coal mines, coal-fired power stations, base-metal smelters, and heavy industry operations (Erbanova et al. 2008, Bohdalkova et al. 2014a). The mountain range near ZL was affected by spruce die-back resulting from SO_x and NO_x emissions during the period of central planning (Oulehle et al. 2017). Air pollution peaked in 1987 in the Czech Republic and around 1990 in Poland (Kopacek and Vesely 2005). Atmospheric S and N deposition decreased following the return of market economy to both countries during the 1990s. The central segments of both peat bogs are unforested and relatively wet. At both sites, bog water pH is between 3.9 and 5.3, and slightly increases downcore. Stagnating water column with little vertical mixing is typical throughout the year. Following major precipitation events, 95% of horizontal water flow occurs in the topmost several centimeters of the *Sphagnum* cover. No groundwater inputs were detected. Nitrogen pools and fluxes at both sites were studied using natural abundance N isotope ratios by Novak et al. (2016).

Fig. 1 Location of the study sites. UDL and LIZ are small upland catchments, situated in the vicinity of the studied peat bogs (BS and ZL) whose input N fluxes via atmospheric deposition were measured by Fottova (1998)

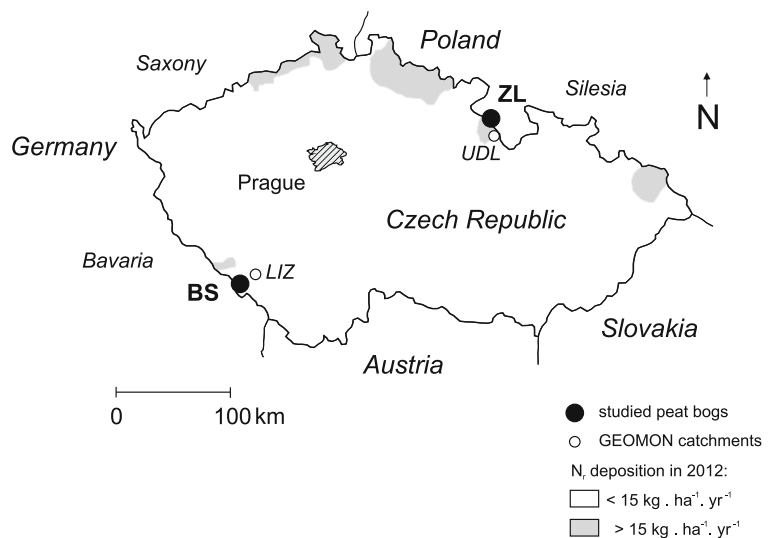


Table 1 Study site characteristics

| Site | Acronym | Location | Elevation (m) | Bog area (ha) | Maximum peat depth (cm) | Precipitation total in 2013 (mm year ⁻¹) | Mean annual temperature (°C) | Predominating <i>Sphagnum</i> species |
|----------------------------------|---------|--------------------------------|---------------|---------------|-------------------------|--|------------------------------|---|
| Blatenská slat, Czech Republic | BS | 48° 58' 33" N 13° 27' 22" E | 1260 | 7 | 700 | 1470 | 3.5 | <i>Sphagnum magellanicum</i> Brid. <i>Sphagnum cuspidatum</i> Ehrh.ex Hoffm. <i>Sphagnum majus</i> C.E.O.Jensen <i>Sphagnum russowii</i> |
| Torfowisko pod Zielencem, Poland | ZL | 50° 20' 52" N 16° 24' 34" E | 750 | 218 | 850 | 1080 | 5.5 | <i>Sphagnum magellanicum</i> Brid. <i>Sphagnum cuspidatum</i> Ehrh.ex Hoffm. <i>Sphagnum papillosum</i> Lindb. |

2.2 Sampling

At each study site, six peat cores, 10-cm in diameter, 15-cm long, were taken in a lawn, avoiding hummocks and hollows. The distance between the two adjacent peat cores was 20 to 40 m. Sampling took place in late April, i.e., 1 month after the end of the snowmelt period. All 12 peat cores were 100% covered with *Sphagnum magellanicum* Brid., and the water table level was 1 to 2 cm below surface. During sampling, care was taken not to drain the porewater; the cores were kept vertically, transported to the laboratory, and placed in a growth chamber (15 °C day, 9 °C night, daylight duration of 14 h per day) for a 2-week acclimation.

2.3 Experimental Design

The design of the peat incubation experiment is summarized in Table 2. Six replicate peat cores per site were randomly divided in a group of three cores that were subjected to the ¹⁵N treatment and a group of three control cores. The surface of each treatment core received 0.087 mg ¹⁵N in the form of water-soluble Na¹⁵NO₃ in one dose at the onset of the incubation experiment. The control cores were incubated with no added ¹⁵N. The peat cores, placed vertically in a growth chamber, were allowed to drain gravitationally through a mesh into a beaker; however, no pore water was recovered at the bottom of the peat cores throughout the 40-week experiment. Bog water from each site was

Table 2 Experimental design of the ¹⁵N peat incubation

| | |
|---|--|
| Total number of incubated peat cores | 12 (6 from each of the two study sites) |
| Moss species | <i>Sphagnum magellanicum</i> Brid. |
| Peat core diameter | 10 cm |
| Peat core length | 15 cm |
| Chemical form of ¹⁵ N | Na ¹⁵ NO ₃ , 98% ¹⁵ N |
| Timing of ¹⁵ N application | Only at the start of peat incubation |
| Amount of ¹⁵ N added per core | 0.081 mg |
| Water table depth | 2 cm below <i>Sp. capitula</i> |
| Amount of surface bog water used for moisturizing | 742 mm year ⁻¹ |
| Incubation temperature | 15 °C (day), 9 °C (night) |
| Daylight duration | 14 h |
| Duration of the experiment | 40 weeks |

used to top up the polyethylene cylinders with peat so that the water table level was kept 2 cm below *Sphagnum capitula* throughout the experiment. The day/night and temperature regime during the experiment (Table 2) was identical to the acclimation period. After 40 weeks, the peat cores were cut into 3-cm segments, dried at 40 °C to a constant mass, and homogenized.

2.4 Analysis

Bog water and peat from BS and ZL were analyzed for major cations and anions using conventional methods (Oulehle et al. 2017). For NO_3^- analysis, HPLC Knauer 1000 was used with a detection limit of 0.3 mg L^{-1} ; for NH_4^+ analysis, a Perkin-Elmer Lambda 25 spectrophotometer was used with a detection limit of 0.02 mg L^{-1} . The detection limits for K and P in peat were 50 ppm. For the N concentration and isotope analysis, two separate 10-mg aliquots of peat were placed in a tin (Sn) capsule and combusted at 1040 °C with copper (Cu) grains and oxides in a Fisons 1108 elemental analyzer. Nitrogen concentrations in peat were determined with a reproducibility of $\pm 1.5\%$. The N isotope compositions were determined on a *Delta V* mass spectrometer coupled with the Fisons 1108 elemental analyzer. Natural abundance N isotope ratios were expressed in the $\delta^{15}\text{N}$ notation as a ‰ deviation of the $^{15}\text{N}/^{14}\text{N}$ composition of the sample from that of a standard (atmospheric N_2). IAEA isotope standards were analyzed every 1-day session (N_1 with a $\delta^{15}\text{N} = 0.5 \text{ ‰}$ and N_2 with a $\delta^{15}\text{N} = 20.3 \text{ ‰}$). Additionally, in-house standards [$(\text{NH}_4)_2\text{SO}_4$ with a $\delta^{15}\text{N} = -1.7 \text{ ‰}$ and glycine with a $\delta^{15}\text{N} = 4.0 \text{ ‰}$] were analyzed following every six samples during each analytical run. The reproducibility of the $\delta^{15}\text{N}$ values of peat was $\pm 0.35 \text{ ‰}$.

The results of the ^{15}N tracer experiment were expressed as the content of ^{15}N atoms in total N atoms. ^{15}N excess values (in atomic ‰) were obtained by subtracting the background ^{15}N of *Sphagnum* or peat from the labeled samples (see Xing et al. 2011 and Zajac and Blodau, 2016 for details).

Statistical analysis was performed using the R software, version 3.4.2 (R Core Team 2017) and the *nlme* package (Pinheiro et al. 2016). The two study sites were compared by the mean of generalized least squares (Pinheiro and Bates 2000), assuming possibly different variability of the outcomes at BS and ZL. The comparison was adjusted for a possible effect of depth. In the following sections, means and standard errors are given.

3 Results

3.1 Chemistry of the Bog Water

Bog water from each site was used as the moisturizing solution during peat incubation. Its chemistry is given in Table 3. Conductivity of the bog water from the historically more polluted site ZL was higher by a factor of three, compared to the less polluted site BS. The ZL bog water was more acidic, compared to the BS bog water (pH of 4.2 vs. 5.3). Concentrations of NO_3^- and NH_4^+ in the bog water were nearly twice higher at ZL than at BS (Table 3). Concentration of SO_4^{2-} in ZL bog water was more than twice higher, compared to BS.

3.2 Peat Density and Ash Content

Statistically, peat bulk density did not differ between the two sites ($p > 0.05$). The mean peat bulk density at BS ($0.049 \pm 0.004 \text{ g cm}^{-3}$) was slightly higher than the mean peat bulk density at ZL ($0.045 \pm 0.002 \text{ g cm}^{-3}$). At both sites, the peat bulk density increased with an increasing depth (Fig. 2a). Cumulative peat mass increased smoothly downcore and was indistinguishable at both sites ($p > 0.05$; Fig. 2b). Ash content at both sites was below 5 wt%, which is the customary upper limit for ombrotrophic peatlands. Significantly more ash was

Table 3 Chemistry of the moisturizing solutions

| | BS | ZL |
|---|--------|--------|
| Na^+ (mg L^{-1}) | 0.48 | 0.27 |
| K^+ (mg L^{-1}) | 0.10 | 0.12 |
| Ca^{2+} (mg L^{-1}) | 0.20 | 0.45 |
| Mg^{2+} (mg L^{-1}) | 0.07 | 0.19 |
| NH_4^+ (mg L^{-1}) | 0.23 | 0.39 |
| Mn^{2+} ($\mu\text{g L}^{-1}$) | < 5.0 | 8.0 |
| Al (mg L^{-1}) | < 0.20 | < 0.20 |
| Fe (mg L^{-1}) | 0.08 | 0.49 |
| Cl^- (mg L^{-1}) | 0.09 | 0.31 |
| SO_4^{2-} (mg L^{-1}) | < 0.30 | 0.80 |
| NO_3^- (mg L^{-1}) | 0.10 | 0.18 |
| HCO_3^- (mg L^{-1}) | 3.1 | 7.3 |
| PO_4^{3-} (mg L^{-1}) | 0.08 | n.d. |
| DOC (mg L^{-1}) | 12.2 | 38.1 |
| pH | 5.25 | 4.17 |
| Conductivity ($\mu\text{S cm}^{-1}$) | 11.6 | 37.3 |

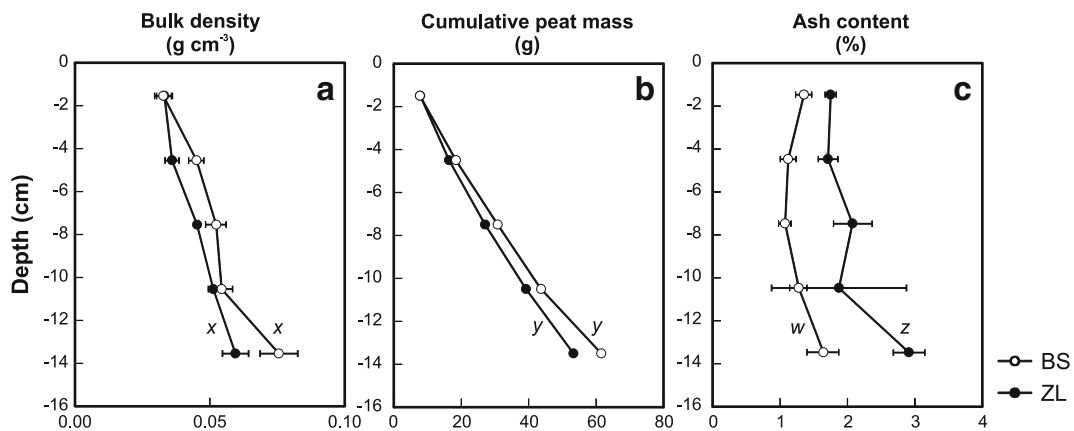


Fig. 2 Peat density, cumulative peat mass, and ash contents. Different letters mark significantly different values for the BS and ZL peat bogs ($p < 0.05$)

found at ZL (2.06 ± 0.22 wt%) than at BS (1.29 ± 0.08 wt%; $p < 0.05$).

3.3 Carbon and Nutrients in Peat

Carbon (C) concentration in peat was significantly higher at BS (42.3 ± 0.3 wt.%) than at ZL (40.7 ± 0.4 wt.%; $p < 0.05$; Table S1 in the Electronic Annex). Nitrogen concentration was statistically indistinguishable at the two sites (0.91 ± 0.04 wt% at BS and 0.84 ± 0.04 wt% at ZL; $p > 0.05$; Table S1 in the Electronic Annex). With an increasing depth, N concentration in peat generally increased (Fig. 3a). C:N ratios were similar at both sites and decreased with an increasing peat depth (Fig. 4a). Phosphorus (P) concentration was significantly higher at ZL (377 ± 29 ppm) than at BS (286 ± 12 ppm; $p < 0.05$; Table S1 in the Electronic Annex). N:P ratios were between 20 (ZL, deeper than 3 cm) and

40 (BS, deeper than 10 cm), with no clear-cut depth gradient. One exception was a sharp downcore decrease in N:P between the two topmost peat samples (Fig. 4b). Potassium (K) concentration was statistically indistinguishable between the two sites ($p > 0.05$). The mean K concentration at BS was 1040 ± 240 ppm, the mean K concentration at ZL was 1180 ± 210 ppm (Table S1 in the Electronic Annex). N:K ratios increased with an increasing peat depth at both sites and were either similar at both sites or higher at BS (Fig. 4c).

3.4 Natural Abundance N Isotope Ratios in Peat

All 30 measured $\delta^{15}\text{N}$ values of bulk peat were negative ($\delta^{15}\text{N}$ of the standard corresponds to N isotope composition of atmospheric N_2 ; $\delta^{15}\text{N}_{\text{std}} = 0$ ‰). The $\delta^{15}\text{N}$ values of bulk peat were significantly less negative at BS (-2.9 ± 0.2 ‰) than at ZL (-3.4 ± 0.1 ‰; $p < 0.05$;

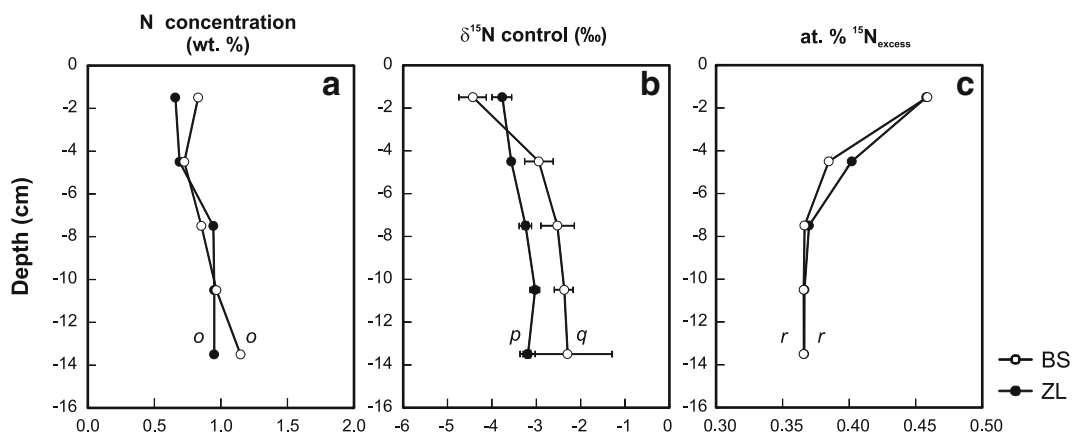


Fig. 3 Nitrogen concentrations, $\delta^{15}\text{N}$ values in intact peat cores, and excess ^{15}N (at.%) at the end of the $^{15}\text{NO}_3^-$ incubation experiment. Different letters mark significantly different values for the BS and ZL peat bogs ($p < 0.05$)

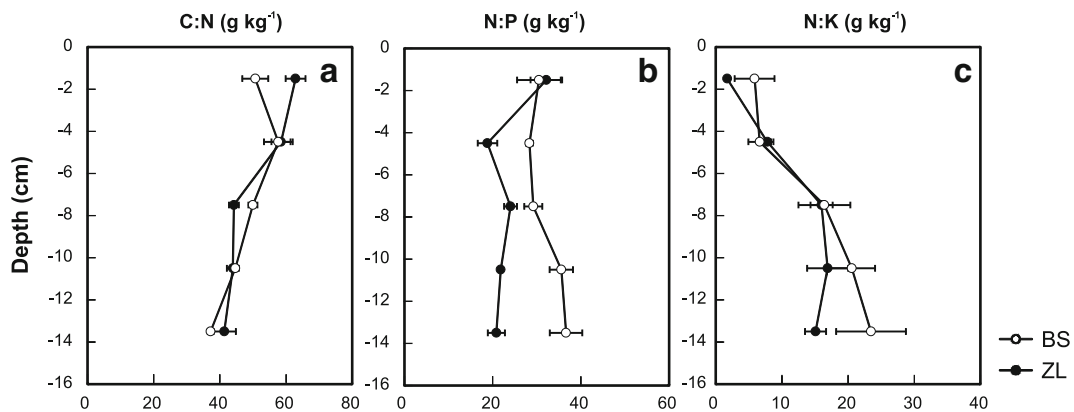


Fig. 4 N:C, N:P, and N:K ratios in peat from BS and ZL

Table S1 in the Electronic Annex). In the shallowest depth interval, $\delta^{15}\text{N}$ values of bulk peat increased more at BS than at ZL. In deeper peat sections, only a very small downcore increase in $\delta^{15}\text{N}$ values was observed (Fig. 3b).

3.5 Downcore Leaching of the $^{15}\text{N}\text{-NO}_3^-$ Tracer in Peat

Total ^{15}N recovery was calculated at the end of the 40-week peat incubation experiment by summing up ^{15}N yields in five 3-cm thick peat segments (depths of 0 to 15 cm below peat surface). As mentioned already in the “Materials and Methods” section, no ^{15}N was leached below the depth of 15 cm. Relative to the amount of $85\ \mu\text{g}$ of ^{15}N applied on the surface of each core at time $t=0$, the ^{15}N recovery in peat at the end of the experiment was $99.6 \pm 0.2\%$.

The result of the ^{15}N tracer experiment is given in Fig. 3c. In incubated peat from both sites, the amount of excess ^{15}N decreased with an increasing depth. This decrease was just slightly faster at BS, compared to ZL (see the second shallowest peat segment, 3–6 cm below surface in Fig. 3c). However, the maximum depth reached by the ^{15}N tracer was the same in peat cores from both sites ($p > 0.05$). Only 2.6% of the ^{15}N tracer was detected deeper than 9 cm below peat surface.

4 Discussion

4.1 Contrasting N Pollution History of BS and ZL

Regional differences in atmospheric N deposition in the Czech Republic have been discussed by Fottova (1995, 2003), Fottova and Skorepova (1998), Fisak et al.

(2002), Oulehle et al. (2011, 2016, 2017), Hunova et al. (2014), and Novak et al. (2014, 2015a,b, 2016). Historical reconstructions of atmospheric N loads in the Czech Republic were performed by Kopacek et al. (2001), Kopacek and Vesely (2005), and Kopacek and Posch (2011). Table 4 summarizes the chemistry of open-area deposition (bulk precipitation) and spruce canopy throughfall in the hydrological year 1995, i.e., at the beginning of hydrogeochemical monitoring in the GEOMON system of small headwater catchments (Fottova and Skorepova 1998). The two sites selected for Table 4 are located close to the currently studied peat bogs; LIZ is located near BS in the southwest, while UDL is located near ZL in the northeast (Fig. 1). In the water year 1995, NO_3^- deposition in clearings at UDL was by a factor of 2.7 higher than that at LIZ. NH_4^+ deposition in clearings at UDL was by a factor of 2.2 higher than that at LIZ. In the same year, throughfall at UDL contained six times more NO_3^- and seven times more NH_4^+ than throughfall at LIZ. Open-area deposition is a better measure of the relative N pollution levels in the two regions, since part of the N in throughfall is leached from the canopy, and some atmospheric N is intercepted by the canopy. Novak et al. (2015a) have shown that horizontal deposition in N-polluted peat bogs adds approximately 30% of N to the vertical deposition in an open area.

Nitrogen deposition in 2013, i.e., in the year of peat sampling for the ^{15}N tracer experiment, was measured directly at BS and ZL (Novak et al. 2016). Figure 5 compares annual N depositions in 1995 and 2013 for both nitrate and ammonium. Whereas total N deposition into BS was generally lower and did not change over the 18-year period, total N deposition into ZL decreased 2.8 times. In 2013, N deposition into the *Sphagnum* cover

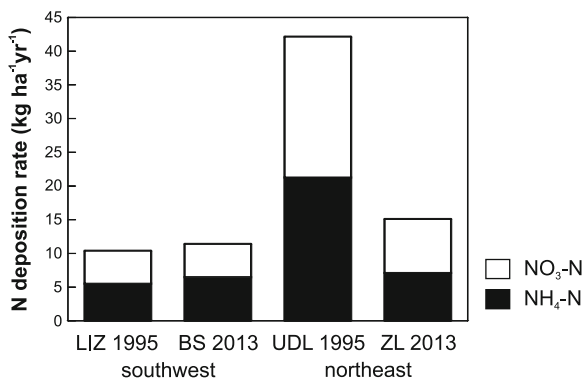
Table 4 Atmospheric deposition in the past high-pollution period in nearby GEOMON catchments (hydrological year 1995)

| | Na ⁺ | K ⁺ | Ca ²⁺ | Mg ²⁺ | NH ₄ ⁺ | Cl ⁻ | SO ₄ ²⁻ | NO ₃ ⁻ | pH |
|---|-----------------|----------------|------------------|------------------|------------------------------|-----------------|-------------------------------|------------------------------|------|
| (kg ha ⁻¹ year ⁻¹) | | | | | | | | | |
| LIZ | | | | | | | | | |
| Open-area deposition | 1.75 | 2.06 | 2.46 | 0.54 | 9.65 | 3.34 | 27.2 | 22.6 | 4.69 |
| Throughfall deposition | 2.75 | 14.2 | 6.34 | 1.90 | 5.25 | 5.49 | 36.2 | 20.0 | 4.51 |
| UDL | | | | | | | | | |
| Open-area deposition | 7.68 | 11.5 | 19.1 | 2.37 | 21.6 | 16.9 | 86.2 | 60.3 | 4.97 |
| Throughfall deposition | 16.6 | 32.8 | 58.1 | 8.27 | 35.8 | 30.6 | 226 | 121 | 4.10 |

was 11.4 kg ha⁻¹ year⁻¹ at BS and 15.1 kg ha⁻¹ year⁻¹ at ZL (Fig. 5). The contribution of NO₃⁻ to total N deposition was about 40% at BS and 60% at ZL (Fig. 5).

As we have seen in Table 3, N concentrations in surface bog water reflect higher pollution at ZL, relative to BS. In 2013, NO₃⁻ and NH₄⁺ concentrations in bog water were less than twice higher at ZL than at BS. This agrees well with the less than twice higher atmospheric deposition at ZL, compared to BS, in 2013 (Fig. 5). A similar pattern was reported by Limpens et al. (2003) and Bragazza and Limpens (2004), who found higher N concentrations in interstitial bog water under higher atmospheric N inputs.

According to the classification by Lamers et al. (2000), present-day BS with 11.4 kg N ha⁻¹ year⁻¹ is a site with low N pollution but close to the lower limit of medium-polluted sites (12 kg N ha⁻¹ year⁻¹), and ZL with 15.1 kg N ha⁻¹ year⁻¹ is a medium-polluted site (i.e., falls within the range of 12–18 kg N ha⁻¹ year⁻¹). In the mid-1990s, ZL was a highly N polluted site (42 kg ha⁻¹ year⁻¹; Fig. 5), while BS was characterized by a low N pollution level (10 kg ha⁻¹ year⁻¹; Fig. 5).

**Fig. 5** Atmospheric deposition of reactive nitrogen in 1995 and 2013. For site location see Fig. 1

4.2 δ¹⁵N Trends in Bulk Peat

Shallow peat cores often exhibit an increase in δ¹⁵N values with an increasing depth (Nadelhoffer et al. 1996, Kuhry and Vitt 1996, Högberg 1997, Novak et al. 1999, 2014, Kalbitz and Geyer 2002, Blodau et al. 2006, Esmeijer-Liu et al. 2012). As seen in Fig. 3b, a downcore increase in δ¹⁵N values of bulk peat was more pronounced at BS than at ZL. Previous literature ascribed this N isotope trend to preferential release of isotopically light (¹⁴N-enriched) nitrogen during the degradation of organic molecules, typical of early stages of peat diagenesis. The BS trend in δ¹⁵N in peat is similar to previously published trends in δ¹³C and δ³⁴S values along vertical peat profiles (Novak et al. 1994, 1999, 2010, Bohdalkova et al. 2014b). Indeed, isotopically heavier C, N, and S in deeper horizons are also typical of aerated forest soils (Nadelhoffer and Fry 1988, Novak et al. 1996). The proposed controlling mechanism is always the same: preferential removal of isotopically light C, N, and S during decomposition of organic matter, with isotopically heavier residual C, N, and S, observed in older/deeper soil layers. We suggest that peat maturation and removal of mobile, low-δ¹⁵N nitrogen were responsible for the BS trend in Fig. 3b. Recently, several studies have shown that temporal changes in environmental parameters also affect δ¹⁵N trends in ageing peat. For example, peat decomposition was faster during periods of higher ash inputs (Broder et al. 2012). Multiple microbial recycling of atmospheric N within the peat profile, availability of other nutrients, such as P, shifts in plant community structure, and land use changes also affect the downcore δ¹⁵N profiles (Kohzu et al. 2003, Limpens et al., 2004, Inglett et al. 2007, Jones et al. 2010, Tfaily et al. 2014, Biester et al. 2014, Kruger et al. 2015). Generally, higher δ¹⁵N values in BS peat at most peat depths, compared to ZL peat

(Fig. 3b), may be related to the fact that microbial N_2 fixation could have played a more important role at BS as the less N polluted site. BS may have experienced a convergence of $\delta^{15}N$ values of bulk peat toward the N isotope signature of atmospheric N_2 (0‰) as a result of N_2 fixation. Microbial N_2 fixation, a thermodynamically costly process, would be less likely at ZL as the more N polluted site. For more detailed discussion of N_2 fixation by *Sphagnum*-dominated wetlands see Larmola et al. (2014), Vile et al. (2014), Novak et al. (2016), and Van den Elzen et al. (2017).

4.3 Nitrogen Mobility in Peat and Downcore Leaching of the ^{15}N Tracer

As we have mentioned in the “Introduction,” peak tropospheric N pollution in the study region dates to the late 1980s and early 1990s. Our ^{15}N incubation experiment took place in 2013, which is 20 to 30 years after the maximum atmospheric N input onto the *Sphagnum* surface. Lead-210 dating at Czech sites repeatedly shows that 20- to -30-year-old substrate is found in rather shallow layers (5–15 cm; Mihaljevic et al. 2006, 2008, Novak et al. 1994, 2008). Such shallow depths coincide with the depth of penetration of ^{15}N in previous tracer studies in highly polluted wetlands (e.g., Heijmans et al. 2002, Nordbakken et al. 2003, Blodau et al. 2006). We hypothesized that shallow peat layers at ZL may contain as little N as analogical shallow peat layers at BS because of the past N saturation at ZL. Indeed, the N concentration in bulk peat at both study sites was indistinguishable (Fig. 3a). Statistically, no peak in N concentration in bulk peat was detected ($p > 0.05$). We conclude that the “excess” N deposited on the *Sphagnum* surface at ZL around 1990, with respect to today’s deposition (Fig. 5), was leached to peat layers deeper than the studied interval of 0–15 cm below surface and/or removed laterally via surface runoff. Some of the excess N could have been emitted as N_2O or N_2 resulting from denitrification (see Novak et al. 2015a,b for data from a peat bog close to ZL). This conclusion is corroborated by Fig. 6 in which we converted peat depth into an age scale. For the purpose of Fig. 6, we interpolated ^{210}Pb ages from 2-cm peat segments (Novak et al. 2017, Table S2 in the Electronic Annex) to 3-cm peat segments. Figure 6a depicts the atmospheric N emissions, dominated by the industrial north of the Czech Republic according to Kopacek and Vesely (2005). Figure 6b plots N concentrations in peat

from BS and ZL in a temporal perspective, and Fig. 6c gives N accumulation rates in individual peat segments, based on N concentrations, peat bulk density, and ^{210}Pb dates. Neither Fig. 6b nor Fig. 6c exhibit the 1990 maximum in atmospheric N emissions seen in Fig. 6a.

In light of the nearly identical vertical N concentration and accumulation patterns in peat from BS and ZL, it may not be surprising that the maximum depth of penetration of the ^{15}N tracer in our incubation experiment was the same at both sites (Fig. 3c). No ^{15}N tracer was detected deeper than 12 cm below surface, and only less than 3% of the tracer were found deeper than 9 cm below surface. Neither of the study sites currently belongs to the “highly N polluted” sites ($> 18 \text{ kg N ha}^{-1} \text{ year}^{-1}$) sensu Lamers et al. (2000). At both sites, green *Sphagnum* plants were present to a depth of 5 cm below surface. Forty weeks after tracer application, most tracer remained in the *Sphagnum* cover (Fig. 3c, two topmost samples).

4.4 Comparison with Previous ^{15}N Tracer Experiments in Freshwater Wetlands

Our experiment differs from previously published ^{15}N tracer studies in that the vertical peat profiles were kept water-saturated. None of the previous studies reported more efficient interception of a ^{15}N tracer in the topmost peat segments, compared to Fig. 3c. Zając and Blodau (2016) studied the fate of ^{15}N nitrate in mesocosms from five peatlands differing in N deposition rates and found that the decline in N retention above atmospheric input of $15 \text{ kg N ha}^{-1} \text{ year}^{-1}$ was more modest than previously thought. After 24 weeks and multiple ^{15}N applications, *Sphagnum* (including *Sp. magellanicum* Brid.) intercepted about one half of the ^{15}N tracer, and 78–98% of the ^{15}N tracer pool in peat were recovered in the top 20 cm of the profile. Because of its lower density, *Sphagnum* continued to be a more efficient filter for the ^{15}N tracer than the underlying peat, even at high atmospheric N depositions of more than $50 \text{ kg ha}^{-1} \text{ year}^{-1}$. The water table level was 28 and 8 cm below the moss layer. Dissolved inorganic N (DIN) contributed less than 1% to the ^{15}N retention, regardless of the N pollution level (Zając and Blodau, 2016). Xing et al. (2011) reported the results of a $^{15}NO_3^-$ tracer experiment in two ombrotrophic peat bogs in Canada. The highest atmospheric N deposition found then in Canada was $15 \text{ kg ha}^{-1} \text{ year}^{-1}$,

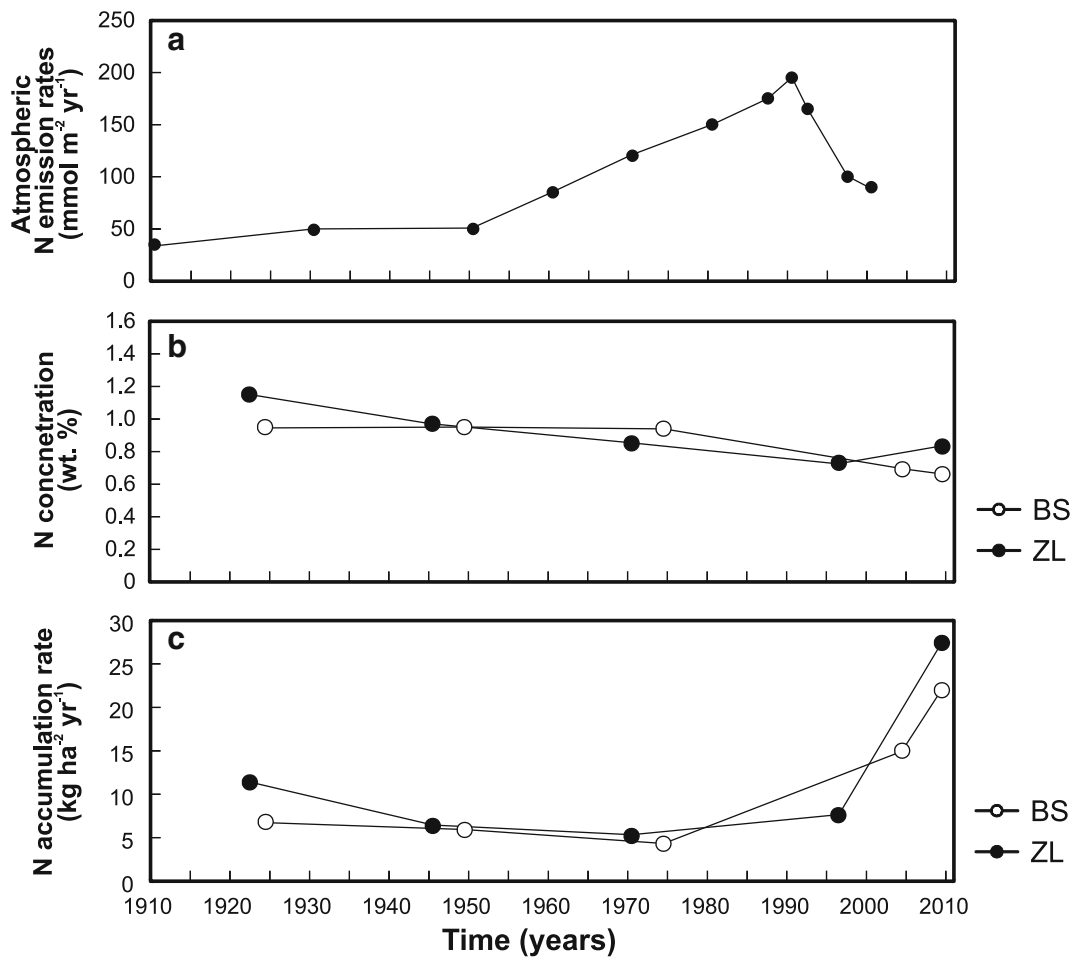


Fig. 6 Historical N emission rates in the Czech Republic, dominated by the industrial north according to Kopacek and Vesely (2005) (a), plot of N concentration in peat vs. age (b), and plot of N accumulation rates in peat vs. age (c)

which is close to the N input at ZL in 2013, the year of our incubation experiment. At the Canadian sites, rapid immobilization of inorganic ¹⁵N by microorganisms and mycorrhizal assimilation was observed. A sharp decrease of the ¹⁵N signal was seen below the depth of 10 cm after 4 weeks. This depth was similar to that in our 40-week-long experiment. ¹⁵N content in the microbial biomass in the Canadian study was lower compared to that in *Sphagnum* and the underlying peat, and cycling of the tracer by microorganisms was fast. The mean residence time of ¹⁵N in microbial biomass was mere 7 days. Xing et al. (2011) also showed that the relative amount of the tracer found in the microbial biomass decreased with an increasing atmospheric N deposition.

Blodau et al. (2006) studied peat receiving 6 and 15 kg N ha⁻¹ year⁻¹. In the experiment, a NH₄¹⁵NO₃

addition increased N input to 15 and 47 kg ha⁻¹ year⁻¹, while the water table was kept 1 and 32 cm below *Sphagnum capitula*. After 14 weeks, substantial ¹⁵N mobility was ascribed to the water table drawdown. Up to 11% of the tracer was found 8 to 12 cm below surface, with up to 99% of the tracer retained in the unsaturated upper zone. At the end of the experiment, only 1% of the ¹⁵N tracer was found in DIN and DON, indicating relative stability of the organic N forms. Blodau et al. (2006) suggested that most downcore N mobility in peat is controlled by particulate organic matter transport. This mechanism is unlikely in our experimental design because of the low hydraulic conductivity in waterlogged peat (Fraser et al. 2001). An important conclusion of the Blodau et al. (2006) study was that even an extremely high

N input of $47 \text{ kg ha}^{-1} \text{ year}^{-1}$ did not compromise the filtering function of the topmost layers of the peatland.

Li and Vitt (1997) working in relatively unpolluted parts of Canada reported that most ^{15}N was immediately sequestered by the moss layer. However, due to an extremely low water table, some tracer was recovered as deep as 40 cm below surface. Nordbakken et al. (2003) found that nearly all N entering the bog was incorporated into the organic matter even when inorganic N input was increased to $40 \text{ kg ha}^{-1} \text{ year}^{-1}$ for a period of 3 years. The ^{15}N label was recovered mainly from the peat depths of 5 and 10 cm below surface, similar to our results (Fig. 3).

Chiwa et al. (2016) suggested that the *Sphagnum* N filter is more compromised when NH_4^+ largely dominates the elevated atmospheric N deposition, compared to NO_3^- . In our experiments (Fig. 3c), we did not study NH_4^+ mobility in peat, however, ammonium did not largely dominate atmospheric N deposition at either study site. Slightly more ammonium N, compared to nitrate N, was deposited at the southwestern less polluted site BS (Fig. 5). It remains to be seen whether this small difference in N speciation in the atmospheric input affects the overall N leaching at BS and ZL. Heijmans et al. (2002) used ^{15}N -labeled ammonium in a peat core experiment with the water table fluctuating between 5 and 20 cm below surface. The ^{15}N tracer applied as ammonium did reach deeper peat layers than in our experiment with ^{15}N labeled nitrate (15 cm vs. < 9 cm), but this greater N mobility in the Heijmans et al. (2002) experiment was likely a result of more aerated peat, compared to our experiment.

Fritz et al. (2014) conducted a combined $^{15}\text{NH}_4^+ / ^{15}\text{NO}_3^-$ study in one pristine and one polluted wetland confirming the conclusion by Nordbakken et al. (2003) that ^{15}N binding at adsorption sites was negligible. The NH_4^+ -N uptake rates by *Sphagnum* moss were initially higher than those of NO_3^- -N, but over time the uptake rates of both N species became similar. Fritz et al. (2014) proposed that long exposure to high N inputs significantly decreases N uptake rates by *Sphagnum* and the underlying peat at all doses. This conclusion is consistent with our interpretation of Fig. 3a and Fig. 6b, c, specifically with the missing accumulation of excess industrial N in 20- to 30-year-old peat layers at ZL. Leaching of N may result from saturation of temporal N storage pools in the vacuoles and cell walls. The concept proposed by Fritz et al. (2014) broadens the

scenarios of Lamers et al. (2000) which specified the bog's response to changing N deposition. There may be no fixed upper threshold of N uptake by *Sphagnum* related to N saturation. Instead, N uptake may decrease over time, regardless of N concentrations in *Sphagnum*, microbes and topmost peat layers.

4.5 Nutritional Constraints in *Sphagnum* Under Different N Inputs

Clearly, the N filter function of *Sphagnum* is influenced by an interaction with other nutrients. Bragazza et al. (2004) argued that at N depositions higher than $10 \text{ kg ha}^{-1} \text{ year}^{-1}$ *Sphagnum* in rain-fed bogs changes from being N limited to P and/or K limited. Specifically, the P limitation occurs under $\text{N:P} > 30$, and $\text{N:K} > 3$. Accordingly, *Sphagnum* at both BS and ZL is currently P limited (Fig. 4b). Older peat layers record N:P ratios greater than 30 only at BS, indicating that P may have not been a limiting nutrient. However, caution must be exercised because diagenesis alters elemental ratios in peat profiles. The N:K ratio in living *Sphagnum* was greater than 3 only at BS (Fig. 3c), indicating K limitation. Historically, N:K ratios were much greater than 3 in both peat profiles but, again, may have been modified by diagenesis. We note that Jirousek et al. (2011) found generally low N:P ratios across numerous *Sphagnum*-dominated sites in Central and Eastern Europe, suggesting that relatively high P availability rather than low N availability prevented P limitation. In general, differences in P and K availability at BS and ZL did not cause nutrient imbalances strong enough to affect downcore ^{15}N leaching in our peat incubation experiment.

5 Conclusions

A 40-week laboratory incubation experiment using replicated peat cores from two Central European peat bogs confirmed our hypothesis that contrasting N pollution history would not affect downcore leaching of a $^{15}\text{NO}_3^-$ trace, as long as today's atmospheric N inputs are similar. The maximum depth of the tracer recovery was the same at both sites. At the end of the experiment, less than 3% of the tracer was found deeper than 9 cm below surface. The low rate of ^{15}N leaching downcore at both sites was a result not only of relatively low present-day atmospheric N inputs (11 and $15 \text{ kg ha}^{-1} \text{ year}^{-1}$ at BS and ZL, respectively) but also of the complete water

saturation of incubated peat cores (the water table was kept at 2 cm below the capitula of *Sp. magellanicum* Brid.). By contrast, most previous field and laboratory studies included a period of water table drawdown which facilitated vertical penetration of the ^{15}N tracer to deeper layers of the acrotelm. Importantly, N contents and accumulation rates in shallow peat layers at ZL, corresponding to the peak pollution period ($> 40 \text{ kg N ha}^{-1} \text{ year}^{-1}$), were as low as those at the significantly less polluted BS. The high atmospheric N_r inputs at ZL 20–30 years ago temporarily compromised the filtering function of *Sphagnum*, and the excess N was leached from the peat profile. Following a decrease to atmospheric N pollution levels comparable to BS, efficient filtering of atmospheric N by *Sphagnum* at ZL has been renewed.

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