The fate of experimentally deposited nitrogen in mesocosms from two Canadian peatlands

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Abstract

In large regions of Europe and North America, peatlands have been exposed to elevated rates of atmospheric nitrogen (N) deposition. We investigated the fate of experimentally added N (NH₄⁺¹⁵NO₃) at two different N loads (1.2 and 4.7 g N m⁻² yr⁻¹) and water tables (1 and 32 cm) in intact cores from two peatlands, located in Central and Eastern Canada. The sites receive an estimated total N load of 0.6 g m⁻² a⁻¹ and 1.5 g m⁻² yr⁻¹, excluding nitrogen fixation. In all treatments, experimentally added nitrate (NO₃⁻) was fully (96–99%) and ammonium (NH₄⁺) mostly (81–97%) retained by the plant cover, mainly consisting of Sphagnum mosses, or in the unsaturated zone below. However, on average only 48% of the ¹⁵N were recovered from the plant cover, and substantial amounts were found in depth layers of 2–6 cm (21–46%) and 8–12 cm (1.4–10.8%) below the moss surface. The amount of ¹⁵N retained also significantly decreased with a lower water table from 56 ± 9% to 40 ± 10%. These findings document a substantial mobility of N, particularly during water table drawdown. Analysis of ¹⁵N by a sequential diffusion procedure revealed a transfer of ¹⁵N from NO₃⁻ into NH₄⁺ and dissolved organic N (DON), but the contents of ¹⁵N in these pools accounted for less than 1% of the total N, natural background subtracted. The mass flux of dissolved ¹⁵N into the peat was small compared to the total mass flux of ¹⁵N. The accumulation of ¹⁵N in the bulk peat must have been caused by a mechanism that was not investigated, possibly by transport of particulate organic N.

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1. Introduction

Northern peatlands cover ca. 4.5 million km² worldwide (Kivinen and Pakarinen, 1981), and play an important role in several global biogeochemical element cycles. They store large quantities of carbon...
(C) and nitrogen (N), which are sequestered into organic matter through the synthesis of plant and microbial biomass. In oligotrophic peatlands, N is mostly retained under low atmospheric deposition rates, and the turnover is dominated by organic forms of the element (Hemond, 1983; Urban and Eisenreich, 1988; Urban et al., 1988). Nitrate is usually absent from pore waters (Waughman, 1980; Hemond, 1983; Urban and Eisenreich, 1988), and denitrification rates are accordingly low (Urban et al., 1988). Due to the prevalent low pH of about 4, there is also little potential for nitrification and denitrification (Urban and Eisenreich, 1988). These findings probably also hold for many minerotrophic northern wetlands (Rochefort et al., 1990; Vitt et al., 1995; Li and Vitt, 1997). N is a limiting nutrient for primary production because of its scarcity in pristine ombrotrophic peatlands (Aerts et al., 1992).

In large areas of Europe and North America, peatlands have been exposed to elevated rates of atmospheric N deposition. In pristine environments, input rates of inorganic N are low (<0.5 g m\(^{-2}\) yr\(^{-1}\)) and mostly provided by natural atmospheric deposition and nitrogen fixation via cyanobacteria associated with Sphagnum mosses and other plants (Waughman and Bellamy, 1980; Schwintzer, 1983). Deposition rates, however, reach up to 1.6 g m\(^{-2}\) yr\(^{-1}\) in eastern Canadian (Moore et al., 2004) and 2.0 to 5.0 g m\(^{-2}\) yr\(^{-1}\) in Central and Northern European peatlands (Lamers et al., 2000).

It has been hypothesized that additional supply of N by atmospheric deposition could entail changes in the N and C cycling in peatlands (e.g. Gorham et al., 1984; Lamers et al., 2000). A state of “N saturation”, as suggested for forest ecosystems (Aber et al., 1989, 1998), characterized by the loss of retention capacity and the predominance of mineral N in the pore water, could be the consequence of such changes in high deposition environments (Lamers et al., 2000). The authors concluded, based on a literature survey and mass balance considerations, that this change will occur at total inorganic N deposition rates of 1.5–2.0 g m\(^{-2}\) yr\(^{-1}\). Some experimental evidence supports this hypothesis (Williams et al., 1999a; Vitt et al., 2003). In analogy to forest ecosystems (Berg and Matzner, 1997), further consequences of elevated N deposition may encompass changes in primary production and organic matter mineralization rates.

The rates and the mechanism by which N is retained in the vegetation are critical for effects of N deposition on biogeochemical processes below the moss cover. So far, several studies have documented long-term increases in N concentrations in Sphagnum mosses, basing their observation on regional depositional gradients (Malmer, 1988; Lamers et al., 2000). Field and greenhouse experiments in low deposition environments demonstrated a temporary increase in primary production rates (Rochefort et al., 1990). The fate of deposited total N (Li and Vitt, 1997; Aldous, 2002a,b), nitrate and ammonium (Williams et al., 1999b) was investigated using \(^{15}\)N as a tracer. Experimental studies also showed that the position of the water table may influence the retention of N in the peat (Williams et al., 1999a) and the export of N to the atmosphere by denitrification (e.g. Regina et al., 1996).

We carried out controlled mesocosm experiments with peatland cores to examine the mechanisms involved in N retention. Our specific objective was to determine to what degree and in what form experimentally deposited N is retained. By adding only \(^{15}\)NO\(_3\), which is the more important source of inorganic N in many heavily polluted peatlands, we also investigated whether nitrate is transformed to ammonium and dissolved organic N (DON), and examined the mobility of these species within the peat soils.

2. Methods

2.1. Sites

We used peat cores from two peatlands in central and eastern Canada. The first site, Mer Bleue (MB) near Ottawa, eastern Ontario, is an open, slightly domed, acidic, and ombrotrophic peatland that is dominated by mosses (e.g. Sphagnum capillifolium, S. angustifolium, S. magellanicum and Polytrichum strictum) and shrubs (e.g. Ledum groenlandicum, Chamaedaphne calyculata, Kalmia angustifolia, Vaccinium myrtillus). The regional wet deposition rate of inorganic N from 1990–1996 was 0.81 g m\(^{-2}\) yr\(^{-1}\) of
which ca. 60% was deposited as nitrate (R. Vet, C.U. Ro, and D. Ord, Environment Canada, Ontario, SOE Bulletin No. 99-3). With the exception of some areas in the Appalachian mountain range, this rate represents the largest N deposition levels in North America (Sisterson et al., 1994). The second site in the Experimental Lakes Area (ELA), near Kenora, northwestern Ontario, is a small acidic and oligotrophic, albeit not fully ombrotrophic peatland located in the northwestern watershed of Lake 239 on the Precambrian Shield (Bayley et al., 1986). The peatland is dominated by black spruce (Picea mariana) and mosses (S. magellanicum, S. angustifolium and Sphagnum fuscum). The regional wet deposition rates of inorganic N from 1990–1996 were similar to natural mid-continental background deposition of approximately 0.3 g N m⁻² yr⁻¹, of which ca. 35 % was deposited as nitrate (Bayley et al., 1986; Bayley and Schindler, 1987).

2.2. Experiments

Sixteen peat cores, 20 cm in diameter and 75 cm long, were randomly collected in PVC tubes from hollows in fall 1999, and a drainage mesh and cap attached at the bottom. The vegetation, consisting primarily of Sphagnum mosses, minor numbers of Polytrichum, a few small specimen of L. groenlandicum, C. calyculata, and K. angustifolia, and some unidentified sedges was left intact (Table 1). The total moss biomass in the mesocosms was between 200 and 600 g m⁻² (dry weight), including lower parts of Sphagnum stems. Pore water samplers (Bev-Line IV, Cole Parmer, 7 mm outer diameter, 3 mm inner diameter, ca. 30 perforations per sampler) were inserted horizontally at 2-cm intervals into the cores. The water table was adjusted with distilled water at 2 to 6 cm below the moss surface and kept constant. The cores were placed in the McGill Phytotron, and the temperature was initially adjusted to 22 °C during the day and 8 °C during the night. After day 50, the temperature was lowered to 12 °C (day) and 8 °C (night) to slow down the abundant Sphagnum growth and the C mineralization rates. The experiment was continued under these conditions for another 173 days. Humidity was kept at 70% rH. Light intensity was adjusted to 250 mol m⁻² s⁻¹. Solution was added with a sprinkler 5 to 6 days a week, and water was manually retrieved at 2 mm d⁻¹ from the base of the mesocosm. The set up of the mesocosms, tests about the hydraulic characteristics, and carbon cycling have been previously described (Blodau and Moore, 2002; Blodau et al., 2004).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Species distribution in the mesocosms used for the deposition experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species/Mesoc.</td>
<td>Mer Blue</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>S. angustifolium</td>
<td>X</td>
</tr>
<tr>
<td>S. capillifolium</td>
<td></td>
</tr>
<tr>
<td>S. fallax</td>
<td>X</td>
</tr>
<tr>
<td>S. fuscum</td>
<td></td>
</tr>
<tr>
<td>S. lindbergii</td>
<td></td>
</tr>
<tr>
<td>S. magellanicum</td>
<td>X</td>
</tr>
<tr>
<td>S. papillosum</td>
<td>X</td>
</tr>
<tr>
<td>S. rubellum</td>
<td>X</td>
</tr>
<tr>
<td>S. russowii</td>
<td></td>
</tr>
<tr>
<td>Polytrichum strictum</td>
<td>X</td>
</tr>
<tr>
<td>Chamaedaphne calyculata</td>
<td>X</td>
</tr>
<tr>
<td>Kalmia angustifolia</td>
<td>X</td>
</tr>
<tr>
<td>Ledum groenlandicum</td>
<td>X</td>
</tr>
<tr>
<td>Maianthum trifolium</td>
<td>X</td>
</tr>
<tr>
<td>Vaccinium oxyccocus</td>
<td>X</td>
</tr>
<tr>
<td>Drosera rotundifolia</td>
<td>X</td>
</tr>
<tr>
<td>Andromeda glaucophylla</td>
<td></td>
</tr>
<tr>
<td>Unidentified sedges</td>
<td>X</td>
</tr>
</tbody>
</table>

For the first 60 days of the experiments, all cores were subjected to the same conditions. The water table
was held at the surface and deposition levels represented background values at the Mer Bleue site. Then, the water table level was lowered to ca. 36 cm below the surface in 8 mesocosms by drainage through a pore water sampler, and the deposition levels was raised according to a fractional experimental design (Table 2). The inflowing solute contained $\text{H}_2\text{O}^+(92/358 \text{ mmol L}^{-1}), \text{SO}_4^{2-} (26/104 \text{ mmol L}^{-1}), \text{NO}_3^- (40/120 \text{ mmol L}^{-1}), \text{NH}_4^+ (40/120 \text{ mmol L}^{-1})$ at two concentration levels, and $\text{Ca}^{2+} (30 \text{ mmol L}^{-1}), \text{Mg}^{2+} (15 \text{ mmol L}^{-1}), \text{Na}^+ (50 \text{ mmol L}^{-1}), \text{K}^+ (5 \text{ mmol L}^{-1})$, and $\text{Cl}^-(150/265 \text{ mmol L}^{-1})$. The lower water tables entailed a decrease in evaporation rates so that water tables temporarily rebounded again in this treatment. We resorted to a permanent drainage at 36 cm. From day 143 to 223, the water table level in the mesocosms was between 0 and 2 cm ($n=8$) and 30 and 33 cm ($n=8$), respectively, below the original moss surface. For the last 95 to 99 days of the experiment we applied NH$_4$NO$_3$ (99%) at the above concentrations. Total deposition was 230 and 690 mg m$^{-2}$ for the low- and high-N treatments.

The experiment was terminated by capping the cores at the top and flushing N$_2$ through the core headspace and unsaturated zone. We then sequentially extracted the pore water from individual depth layers through the pore water samplers from the top downwards until field capacity in a layer was approximately reached. The cores were then extracted and cut into 4-cm segments in a glove box under a N$_2$ atmosphere. A portion was sealed in plastic bags and stored at 4 °C for extractable organic, microbial N and inorganic N determinations. The remainder was dried at 70 °C and ground, beginning with the lowermost segments to avoid contamination from the upper layers.

Nitrogen retention was calculated by subtracting the vertical mass flux of a species at the water table and outflow, respectively, from the mass flux by deposition onto the mesocosms. These fluxes ($J$) of species $i$ were calculated as

$$
Retention = J_{i(\text{in})} - J_{i(\text{water table, outflow})}
$$

with $J_i = Q \cdot C_i$ and $Q$ water flux (L m$^{-2}$ d$^{-1}$) $C_i$: measured concentration at that depth (mmol L$^{-1}$) and converted into units of mg m$^{-2}$ d$^{-1}$.

### 2.3. Chemical analyses

Peat C and N concentrations were analyzed using an Elementar vario EL analyzer (Tabatabai and Bremer, 1990). Samples were dried to constant mass at 70 °C, weighed and the dry bulk density calculated. Fumigation with CHCl$_3$ and extraction with 0.5M K$_2$SO$_4$ was carried out with slight modifications according to Voroney et al. (1993). Briefly, approximately 40 g of peat (wet weight) from each bulk sample split into two 20 g samples. One sample was placed in a vacuum dessicator and fumigated with ethanol-free CHCl$_3$ in absence of light for 24 h. Chloroform vapor and residue was then removed through repeated evacuation. All samples were sealed in plastic containers containing K$_2$SO$_4$ solution, shaken for 1 h at 200 RPM on an oscillating shaker, and filtered with 0.45 μm glass fiber filters. A sub-sample of each extract was used in an alkaline persulfate oxidation reaction according to Williams et al. (1995) for determination of total N in solution as NO$_3^-$. Dissolved inorganic N (DIN) was measured as NH$_4^+$ and NO$_2^-+NO_3^-$ using colorimetric methods on a Latchat FIA’8000 series continuous flow auto-analyzer.

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### Table 2

Fractional factorial design matrix of the mesocosm experiment (treatments) and retention of added $^{15}$N-NO$_3^-$ in the living vegetation, and as NO$_3^-$ and NH$_4^+$ in the pore water at the water table and in the outflow of the mesocosms, expressed as a percentage of that added.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Vegetation</th>
<th>Pore-water at water table</th>
<th>Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Location$^a$</td>
<td>WT$^b$</td>
<td>N$^c$</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td>Low</td>
<td>Low</td>
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<tr>
<td></td>
<td>MB</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>ELA</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>ELA</td>
<td>Low</td>
<td>High</td>
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<td>ELA</td>
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<td>Low</td>
</tr>
<tr>
<td></td>
<td>ELA</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

Retention rates of $^{15}$N in the vegetation were calculated from the content in the vegetation, divided by the period of $^{15}$N application. Retention rates of NO$_3^-$ and NH$_4^+$ were calculated according to Eq. (1).

$^a$ MB- Mer Bleue, ELA - Experimental Lakes Area 239.

$^b$ Water table- High 1 cm and Low 32 cm below surface.

$^c$ N additions- Low 1.57 and High 4.70 g N m$^{-2}$ yr$^{-1}$ as NH$_4$NO$_3$. 

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Dissolved organic carbon (DOC) was measured with a TOC analyzer (below) after pH adjustment to 2.5 and sparging with CO\textsubscript{2} free N\textsubscript{2} for 10 min. Extractable DOC and DIN were measured directly in extracts from the non-fumigated samples. Extractable organic N was calculated as total extractable N from the non-fumigated sub-samples minus the DIN. Microbial biomass C and N were calculated by subtracting the non-fumigated extractable DOC and total N from the fumigation-extraction DOC and total N, respectively. No extraction efficiency coefficients were used in our calculations as we were interested in differences among samples, dissolved organic matter (DOM) and microbial biomass C:N quotients, and because there have been reports of a large range of C and N extraction efficiency coefficients (Brookes et al., 1985; Sparling et al., 1990) for different soils.

2.4. Isotope analyses

Total \textsuperscript{15}N was determined on the dried, ground, and homogenized plant-cover and peat material from individual depth layers of the cores via thermal decomposition of the sample material in an elemental analyzer. The produced N\textsubscript{2} was flushed through a gas source isotope ratio mass spectrometer (Finnigan MAT delta plus XL) in continuous flow mode. To determine N isotope ratios in the collected pore water, a sequential diffusion procedure was used, separately trapping individual samples for ammonium, nitrate, and DON (Brooks et al., 1989). Glass containers (350 mL) were prepared with an acid trap able to capture ammonia. The acid trap consisted of 7-mL diameter disks of Whatman GF/D filter paper, cut with a paper punch and pierced with steel wires. Ten \mu L of KHSO\textsubscript{4} (3.5 M) were pipetted onto each disk before beginning the diffusion procedure. The capacity of the traps was >350 \mu g N (Brooks et al., 1989) and was never fully consumed in the experiments. The solutions were transferred to the containers, and 0.5 g of MgO and a glass bead were added to each solution. The wire and disk were mounted, the lid was closed, and the assay was allowed to equilibrate for 12 days at room temperature. After recovery of the disks containing NH\textsubscript{4}-N, 1 mL of 30 mM NaNO\textsubscript{3} solution of known isotopic composition was added to each container to raise the concentration of nitrate to recoverable levels. 0.5 g of Devarda’s alloy was added, a new trap prepared, mounted and the lid closed. After 12 days, the disks containing NO\textsubscript{3}-N were recovered again and the remaining solution was subjected to a Kjehldahl digestion. 5–10 mL of concentrated H\textsubscript{2}SO\textsubscript{4}, 4 g K\textsubscript{2}SO\textsubscript{4}, and 0.5 g CuSO\textsubscript{4} were added to every 70 mL of solution and boiled at 380–400 °C for 3 h. The digest was filled back in the containers, neutralized with NaOH, and used for another set of diffusion assays. The assays were again allowed to equilibrate for 12 days and DON-N was recovered for isotope analysis. Nitrogen isotope ratios of the trapped nitrogen were determined on a Carlo Erba NA 1500 coupled to a Finnigan MAT deltaD mass spectrometer at the Central Analytical Department of the Bayreuth Institute of Terrestrial Ecosystem Research (BITOEK).

The \textsuperscript{15}N results of the tracer experiments are expressed as % of total N, with the respective \textsuperscript{15}N background subtracted (plants: 0.3708%, total N of peat: 0.3677%; traps: 0.3628%). \textsuperscript{15}N isotope measurements of natural abundance are expressed using the delta scale:

\[
\delta^{15}N[\%o] = \left( \frac{^{15}N/^{14}N_{sample}}{^{15}N/^{14}N_{reference}} - 1 \right) \cdot 1000.
\]

The primary reference for nitrogen isotope abundance measurements is atmospheric N\textsubscript{2}. For these analyses the reference materials IAEA-N-1 (+0.43‰) and IAEA-N-2 (+20.32) were repeatedly analyzed for calibration and normalization purposes. The analytical uncertainty was \pm 0.2‰. The analytical uncertainty for measurement of isotopically labeled nitrogen, determined by comparison with reference plant material (beech and spruce leaves) was \pm 2‰.

3. Results

3.1. Total N, C/N quotients, and natural abundance N isotope ratios

Total N in the mesocosm peat increased from 7 to 12 mg N g\textsuperscript{-1} of total dry mass in the surface layers to 12–18 mg N g\textsuperscript{-1} at larger depths (Fig. 1). Only a small fraction of the total N was in the form of microbial N, ranging from <0.05 to 0.5 mg N g\textsuperscript{-1}. In contrast to total N, microbial N contents strongly
decreased with depth in mesocosms from both sites (Fig. 1). C/N quotients of the peat varied considerably between individual mesocosms, ranged from 25 to 60 and, on average, decreased with depth (Fig. 2). At the end of the experiments, we recorded C/N quotients of the plant cover between 40 and 60, with average ratios of 45.7 ± 4.9 (Mer Bleue) and 49.3 ± 9.7 (ELA). Differences in C/N ratios between the N-treatments were small (Fig. 3), and not significant when low and high N treatments were compared. The C/N quotients of the K2SO4-extractable DOM were considerably lower than for the total peat and plant material, and ranged from 10 to 25 (Fig. 2). The average C/N quotient of the microbial biomass was lowest and ranged from 8 to 15 throughout the profiles. The natural abundancy of 15N for peat was only recorded for the MB site. With depth, δ15N values increased from a minimum of −4.6‰ to a maximum of 2.6‰ (Fig. 4). The pattern in the peat was consistent for two replicate cores and other Mer Bleue samples (Moore unpublished data). Different sources of organic matter at the site (C. calyculata stems and leaves, E. vaginatum, Sphagnum spp.) varied in δ15N values for total N from −5.5 to −1.1‰ (Fig. 4). These values somewhat differ from
repeated $^{15}$N abundance measurements of various sources at the site, with *Sphagnum* having values of $-3$ to $-4\,\%$, sedges of about $2\,\%$, and shrub leaves of $-7$ to $-10\,\%$ (Moore, unpublished).

### 3.2. Retention of added nitrate and ammonium

From inflow concentration levels of 120 and 40 $\mu$mol L$^{-1}$, respectively, nitrate concentrations decreased to $<3\,\mu$mol L$^{-1}$ at the water table and beneath in all mesocosms. Concentrations were mostly under 1 $\mu$mol L$^{-1}$ . Nitrate was thus effectively retained above the water table in all treatments (Table 2). Small quantities of nitrate were also found in the K$_2$SO$_4$ extracts (0.01–0.2 $\mu$mol g$^{-1}$) below the water table. At the beginning of the experiment, before the factorial experimental design had come into effect, ammonium concentrations in the soil solution generally increased with depth from ca. 10 $\mu$mol L$^{-1}$ to 50–100 $\mu$mol L$^{-1}$ in the MB mesocosms, and from ca. 5 $\mu$mol L$^{-1}$ to 50–150 $\mu$mol L$^{-1}$ in the ELA mesocosms. After equilibration, at the end of the experiments, ammonium concentrations ranged from 5 to 40 $\mu$mol L$^{-1}$ (Fig. 5). Ammonium was thus also retained by the vegetation, but to a lesser extent (58–97%, Table 2) than nitrate. Below the water table, ammonium was on average released in the low, but not in the high water table treatments (Fig. 5B). On average, between 30 and 400 $\mu$mol g$^{-1}$ of ammonium were extracted with K$_2$SO$_4$. The amount of extractable ammonium strongly decreased with depth (Fig. 5A).

### 3.3. Retention and transformation of added $^{15}$N

At the end of the experiments, between 0.75% and 8.0% (average of both sites: $3.1 \pm 1.8\%$) of the total N in the plant cover, almost exclusively mosses, consisted of the added $^{15}$N. The retention of added $^{15}$N in the plant cover was considerably lower than determined for the DIN at the water table (Table 2). Of the applied $^{15}$N, on average $48.7 \pm 14.2\%$ (MB) and $46.9 \pm 11.4\%$ (ELA) were recovered from the plant cover. Substantial quantities (20–46%) of the applied $^{15}$N were recovered from the total N pool in the peat layer just below the moss cover. Below a depth of 12 cm, only $<5\%$ of the added $^{15}$N was detected, but the isotopic signal remained elevated compared to background values down to the bottom of the mesocosms. The two N-treatments did not differ in their N retention efficiency. Mesocosms subjected to the high water table treatment retained
the applied $^{15}$N on average more effectively (t-test, $^{*}P<0.05$), compared to those with the low water table treatment ($56 \pm 9\%$ vs. $40 \pm 10\%$, Table 2). An exception to this pattern was the high N, low water table treatment of the ELA mesocosms, which retained about the same quantity as the high N, high water table treatment (Fig. 6).

Not all of the recovered traps for the determination of the $^{15}$N contents of nitrate, ammonium, and DON contained enough N for an isotopic analysis. In the three analyzed high N, high water table treatment mesocosms, the recovered nitrate in the surface peat mostly consisted of $^{15}$N (Fig. 7). $^{15}$N in nitrate then decreased with depth to contents $\leq 10\%$ of total N. In two analyzed low N treatments the recovered nitrate only contained traces of added $^{15}$N. $^{15}$N contents of ammonium and DON were clearly elevated compared to background $^{15}$N contents. Up to a maximum of 1.2% of the total N consisted of $^{15}$N, natural background contents subtracted. $^{15}$N had, therefore, been transferred from nitrate to ammonium and DON. In some instances, a peak of the $^{15}$NH$_4^+$-N signal below the water table was observed (Fig. 7A). In all cases, the $^{15}$N contents of ammonium and DON were substantially smaller than $^{15}$N contents of the respective plant cover but, below a depth of 6 cm, always larger than the $^{15}$N content of the total peat.

3.4. Effects of experimental treatments

The two different N-treatments generally induced no clear effect on any of the determined nitrogen pools in the peat. Some differences between the treatments occurred in the upper layers of the mesocosms with respect to the C/N ratio of the extractable DOM (Fig. 2), and concentrations of the extractable ammo-
Differences between parameters primarily occurred between the mesocosms of the ELA and MB site. This was also confirmed by the visual examination of normal distribution plots of the factorial effects. In MB mesocosms, the concentrations of extractable ammonium were significantly smaller (paired t-test, *P* < 0.05) by a factor 2–5 times than in the ELA mesocosms. This finding is qualitatively reflected in the dissolved ammonium concentrations, which were mostly larger in the ELA mesocosms (Fig. 5). The sites also differed with respect to concentrations of microbial N, which were higher at the ELA site in the upper 30 cm of the peat soil as well (Fig. 1).
4. Discussion

4.1. Nitrogen saturation

Overall, the results of this mesocosm study are in agreement with the hypothesis of Lamers et al. (2000) that N saturation will only occur in peatlands that receive more than ca. 1.5–2.0 g N m\(^{-2}\) yr\(^{-1}\). Wet deposition rates at the two investigated sites were well below such values. Other sources of N have to be considered, though. These sources are organic N deposition, dry deposition, and N\(_2\) fixation. DON forms a variable proportion of atmospheric N deposition and may increase the overall deposition by about 50% above the wet deposition (Cornell et al., 2003). Dry deposition is difficult to measure and estimate and may be smaller in open bogs than forests, because of the small surface area: at Mer Bleue, for example, the vascular Leaf Area Index is 1.3 (Moore et al., 2002). Previously, it was assumed that ca. 30% of the total deposition at continental forested peatlands was dry deposition (Urban and Eisenreich, 1988). Thus, contemporary total N atmospheric deposition, N\(_2\) fixation not taken into account, may be 75–100% larger than wet deposition, amounting to about 0.6 g N m\(^{-2}\) yr\(^{-1}\) at the Central-Canadian ELA 239 site, and to about 1.5 g N m\(^{-2}\) yr\(^{-1}\) at the Mer Bleue site in eastern Canada.

Our results confirm that these deposition levels have not impaired the filter function of the moss cover at experimental deposition rates of up to 4.7 g N m\(^{-2}\) yr\(^{-1}\), and did not cause N saturation at the sites. In the experiments, nitrate was effectively retained by the moss layer (Table 2). Ammonium was mostly, although not completely, retained. In some instances net ammonium production was observed during the anaerobic decomposition of organic matter, particularly when the water table was low (Fig. 5). Within the limitations of the experimental approach adopted, the effective retention of inorganic N above the water table suggests that fast and direct effects of additional N deposition on biogeochemical processes in the peat of ombrotrophic bogs cannot be expected at the N deposition levels currently occurring in most of North America. Accordingly, no clear effects of experimental N deposition levels on microbial C/N ratios, exchangeable pools of ammonium, and carbon exchange (Blodau et al., 2004) could be identified in our experiments, although this finding may be due, in part, to the large heterogeneity among the peat cores.

4.2. Nitrogen retention and mobility

The observed retention of N in the mesocosms was in agreement with a longer-term preservation of N in the system. On a per mass basis, extractable ammonium and microbial N were concentrated near the surface and C/N ratios of the extractable DOM were also smallest in the surface layer, although the C/N ratio of the bulk peat was largest. These results, also with respect to the magnitude of the measured concentrations of microbial N, are similar as in the study by Williams and Silcock (1997) in a raised mire in northeastern Scotland receiving a wet deposition of 0.6 mg N m\(^{-2}\) yr\(^{-1}\). The capacity of Sphagnum mosses to relocate N from aging parts to the apices of the plants may have assisted in this preservation of N in the surface layer (Malmer, 1988). In four bogs in the northeastern United States, N relocation ranged from 11% to 83% of the total N required for synthesis of Sphagnum biomass (Aldous, 2002a,b).

A relative preservation of N at lower depths was also suggested by decreasing C/N quotients with depth. On long time scales, C had been lost at a faster rate from the system than N, as documented for other peatlands (e.g. Damman, 1988; Kuhry and Vitt, 1996; Moore et al., 2004). Small continuous losses of N from the peat, due to export of ammonium and DON also occurred in the mesocosms would be in agreement with the background \(\delta^{15}\text{N}\) profiles. In the sampled depth range, the profiles suggested a slow accumulation of \(^{15}\text{N}\) with increasing age of the peat at the Mer Bleue site. This effect could be caused by isotope fractionation during the mineralization process, preferentially mobilizing \(^{14}\text{N}\). The remaining organic matter would then be progressively enriched in \(^{15}\text{N}\) (Gebauer and Schulze, 1991).

It is currently debated whether changes in water tables have an influence on nitrogen retention in nutrient poor peatlands (Aldous, 2002a,b). According to the nitrate and ammonium mass balances, the retention of inorganic N was not decreased by a lower water table level (Table 2), despite reduced rates of photosynthesis and moss growth in the mesocosms (Blodau et al., 2004). The \(^{15}\text{N}\) recovery, on the other hand, suggested a decrease in retention of N from an
observed a decrease in nitrogen retention by plants in the northeastern United States for two years, also in the drier year. Nitrogen transformation and transport remained well below the 15N contents in the plant cover, and was retained in, or lost from the unsaturated zone, for example by denitrification (Regina et al., 1996; Dowrick et al., 1999). Although the N retention did not change when the entire peat profile was considered, the reduced retention of 15N suggests that lower water tables may increase the N supply below the moss canopy. These findings confirm results from earlier greenhouse experiments carried out by Williams et al. (1999a). Aldous (2002a, b), who added 15N to field plots in 4 ombrotrophic bogs in the northeastern United States for two years, also observed a decrease in nitrogen retention by Sphagnum mosses in the drier year.

4.3. Nitrogen transformation and transport

According to the recovery of 15N in DIN and DON, nitrate was converted to ammonium and DON. At least some nitrate was apparently directly reduced to ammonium, as was previously documented by Hemond (1983). This can be concluded as the 15N contents in the ammonium were larger than in the DON and the bulk peat. The occurrence of other transformation processes could not be confirmed, though. 15N contents of the ammonium and DON were very small just below the plant cover, and remained well below the 15N contents in the Sphagnum itself. It seems as if very little DON was leached from Sphagnum that had previously assimilated 15N-NO3-. Organic nitrogen stemming from Sphagnum biomass apparently was not ammonified, nor was synthesized and stored ammonium (Press and Lee, 1982) released to a measurable extent.

Despite the strong retention of inorganic N by the plant cover, the study revealed a substantial mass transfer of 15N into the bulk peat. The significance of this transfer lies in its ability to change the chemical composition of the peat organic matter faster than possible by a purely physical burial of litter. A transfer of this kind was previously found after the experimental field application of 15N in an ombrotrophic bog and a minerotrophic rich fen in western Canada (Li and Vitt, 1997) and in ombrotrophic bogs in the northeastern United States (Aldous, 2002b). In these studies, the potential transfer mechanism could not be investigated because not all relevant species were determined. As a drawback of experimental realism, in field experiments it is furthermore very difficult to quantify below-ground water and material fluxes. At the expense of some realism, a mesocosm study provides the opportunity to overcome these hurdles at least partly. Knowing the advective water flux, and restricting the water flow to one dimension, we estimated a vertical mass transfer of DIN and DON, and compared it to the total 15N mass flux in the peat. These estimates are illustrated by a schematic of one of the Mer Bleue mesocosms (Figs. 7A and 8), and show that the transport of DIN and DON cannot account for the observed nitrogen mass transfer.

At a depth of 2 to 6 cm, the bulk peat contained about 0.8% of 15N above background levels, amounting to 172 mg m⁻², or 24%, of the total applied 15N. The total mass transfer resulting from this concentration, averaged over the period of application, was 1.77 mg 15N m⁻² d⁻¹. While the 15N content of the nitrate was 100%, the low concentration of 2.4 μmol L⁻¹ at the water table entailed only a negligible mass flux of nitrate into this layer (0.092 mg 15N m⁻² d⁻¹). With respect to ammonium, the content of 15N (0.17%) was even lower than in the bulk peat. The mass flux of 15N-NH₄⁺ was hence negligible as well (4.5·10⁻⁴ mg 15N m⁻² d⁻¹). 15N contents of DON were not available for this layer. They were below 1% of the total DON in other cores at that depth, and amounted only to 0.26% of the total DON in the 8 to 12 cm depth interval. Based on a DOC production rate of 46.2 nmol cm⁻³ d⁻¹ in this layer (Blodau et al., 2004), a C/N ratio of the extracted DOM of 9.0 in this particular core, and assuming a 15N content of 1%, a total mass transfer of 0.031 mg 15N-DON m⁻² d⁻¹ would have taken place. Nitrate, ammonium, and DON fluxes in the pore water thus do not explain the mass transfer of 15N into this peat layer. A similar conclusion can be drawn for the layer at a depth of 8 to 12 cm, whose total N stock contained an additional 0.11% 15N, amounting to 5% of the 15N applied to the mesocosm. In other words, the majority of the 15N...
was transferred into the peat by a mechanism not analyzed in this study. The outlined magnitude of nitrogen transfer may be an overestimate, compared to transfer rates under field conditions, because vertical advection rates of groundwater in peatland soils are usually smaller than in this experiment. In peatland soils, water flow patterns are mostly horizontally oriented, as hydraulic conductivity strongly decreases with depth (Fraser et al., 2001). In contrast, the water flow was vertically oriented in our experiment. However, based on the $^{15}$N depth profiles by Li and Vitt (1997) and Aldous (2002b), the described $^{15}$N transfer also seems to occur under field conditions.

The mechanism causing the transfer cannot be clarified without further investigations. A physical artifact seems to be an unlikely explanation, since the tracer application only began after an equilibration period of about 5 months. Preferential flow in the mesocosms was also moderate (Blodau and Moore, 2002). A plausible mechanism would be the transport of particulate organic N. Particulate organic N must have been produced in form of Sphagnum debris, algae, fungal and microbial biomass. Colloids and microbial cells, and thus also microbial N, are transported in other porous media, such as sediments and aquifers (e.g. Harvey et al., 1995). We are unaware of studies that have explicitly addressed particulate organic matter transport in peatland soils.

5. Conclusions

Experimentally added nitrate was fully, and ammonium mostly retained in the Sphagnum dominated plant cover, or in the unsaturated zone above the water table. The results are in agreement with the notion that ombrotrophic peatlands are not saturated with N under the estimated atmospheric N deposition rates of 0.6 to 1.5 g m$^{-2}$ yr$^{-1}$. This range covers most of the depositional gradient across North America. A number of observations, however, argue for a higher mobility of N than might be expected. Of the applied $^{15}$N, on average only 48% could be recovered from the plant cover. Less $^{15}$N was even retained when the water table was low. In northern peatlands, N might thus be particularly mobile during summer droughts. Also, more $^{15}$N was recovered from the peat than could be explained by advective transport of DIN and DON. Nitrate and ammonium concentrations in the pore waters were low, and the transfer of applied $^{15}$N-nitrate into ammonium and DON was fairly insignificant.

Thus, the applied N entered the peat by a mechanism that was not investigated in this study. We speculate that transport of particulate organic N was responsible for this phenomenon.

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