



Fate of N in a peatland, Whim bog: immobilisation in the vegetation and peat, leakage into pore water and losses as N₂O depend on the form of N

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Abstract. Peatlands represent a vast carbon reserve that has accumulated under conditions of low nitrogen availability. Given the strong coupling between the carbon and nitrogen cycles, we need to establish the consequences of the increase in reactive nitrogen deposition for the sustainability of peatlands, and whether the form in which the nitrogen is deposited makes a difference. We have addressed these questions using a globally unique field simulation of reactive N deposition as dry deposited ammonia and wet deposited reduced N, ammonium and oxidised N, nitrate, added as ammonium chloride or sodium nitrate, to an ombrotrophic peatland, Whim bog in SE Scotland. Here we report the fate of 56 kg N ha⁻¹ yr⁻¹ additions over 10 yr and the consequences. The effects of 10 yr of reactive N additions depended on the form in which the N was applied. Ammonia-N deposition caused the keystone *Sphagnum* species, together with the main shrub *Calluna* and the pleurocarpous mosses, to disappear, exposing up to 30 % of the peat surface. This led to a significant increase in soil water nitrate and nitrous oxide emissions. By contrast wet deposited N, despite significantly reducing the cover of *Sphagnum* and *Pleurozium* moss, did not have a detrimental effect on *Calluna* cover nor did it significantly change soil water N concentrations or nitrous oxide emissions. Importantly 10 yr of wet deposited N did not bare the peat surface nor significantly disrupt the vegetation enabling the N to be retained within the carbon rich peatland ecosystems. However, given the significant role of *Sphagnum* in maintaining conditions that retard decomposition, this study suggests that all nitrogen forms will eventually compromise carbon sequestration by peatlands through loss of some keystone *Sphagnum* species.

1 Introduction

Peatlands and bogs are valuable carbon (C) stores and therefore potential C sinks (Belyea and Malmer, 2004). Northern peatlands have accumulated 270–455 Pg of C since the last ice age (Gorham, 1991). Organic, peat soils are the product of C sequestration, a consequence of C assimilation exceeding rates of decomposition. The ability to sequester C underpins their existence and sustainability. Thus, the often cold, acidic, anoxic environments that characterise many peat ecosystems and slow down decomposition rates are fundamental to maintaining their status quo. However, anthropogenic activities can challenge the manifestation of these properties and undermine the ability of peat bog ecosystems to fulfil their role as C sinks (Gunnarsson and Rydin, 2000), especially where change influences the drivers that control C and nitrogen (N) cycling. Changes in water table through drainage, climate or species composition, the latter often observed in response to N eutrophication, (Berendse et al., 2001) are particularly likely to influence C exchange, both via the uptake of carbon dioxide (CO₂) and the release of methane (CH₄). Increases in anthropogenic N deposition can increase productivity and C assimilation but also release C if decomposition rates are accelerated through changes in N availability or species composition (van Breeman, 1995a). The overall consequences of enhanced N deposition for vegetation, function and sustainability and its fate in peat bogs are not fully understood.

The peat bog ecosystem is likely to be highly sensitive to enhanced N inputs, because its stability, with respect to the characteristic plant and microbial species assemblages, has evolved its homeostasis under conditions of restricted

N availability (Bobbink et al., 1998). Increasing deposition of reactive N to these ecosystems will shift the competitive balance between species in favour of those that can exploit the enhanced reactive N supply, with implications for above- and below-ground C and N assimilation and greenhouse gas production (Bouwman et al., 2009). When N deposition exceeds plant demand for N in the short term, the additional mineral N may be used by soil microbes, nitrate (NO_3^-) providing an electron acceptor (Regina et al., 1996), which via denitrification can lead to enhanced emissions of the greenhouse gas nitrous oxide (N_2O) (Sylvan et al., 2002). In the more acidic conditions associated with peat bogs, ammonia oxidising archaea and bacteria may play a significant role in denitrification (Nicol et al., 2008). However, denitrification, assimilating nitrate (NO_3^-) through to release as N_2 , is unlikely in such acidic conditions (Simek and Cooper, 2002).

Deleterious effects of reactive nitrogen (N) deposition on sensitive components of semi-natural ecosystems, e.g. non-vascular plants, are now well described, particularly with respect to reductions in species richness (Bobbink et al., 2011). However, effects on keystone components of N-sensitive habitats and the significance of potential losses, replacement of such species or changes in the balance between functional groups for biogeochemical cycling are less well quantified, except for work on Canadian bogs, particularly Mer Bleue (Bubier et al., 2007; Juutinen et al., 2010; Wendel et al., 2011). Changes in vegetation composition can have important implications for key processes within the ecosystem and ecosystem services. *Sphagnum* mosses perform functions akin to engineers in peatlands (van Breemen, 1995b), generating acidic and nutrient-poor conditions that restrict decomposition, promote C accumulation and remove base cations and other nutrients to maintain low nutrient conditions that help constrain vascular plant growth (Clymo, 1963; Clymo and Hayward, 1982). Mosses, generally, can immobilise a significant proportion of the incoming N deposition helping to regulate its effect on N cycling and availability (Curtis et al., 2005). In the absence of this biological control over reactive N concentrations, vascular plants can become dominant (Bobbink et al., 1998) and the system may start to “leak” (Sylvan et al., 2002). Limits to the effectiveness of *Sphagnum* and other mosses in these roles in the presence of reactive N deposition do exist (Lamers, 2000). However, we do not know to what extent the form of N in deposition influences such processes.

Despite the obvious potential for N deposition to significantly affect the basic ecosystem services that peatlands provide, there have been few realistic *in situ* N manipulation experiments to quantify N-driven effects, and none that have checked whether the form in which N deposits is important. Demonstrating whether the form of N deposition matters is important for the following reasons: (1) the sources differ, with reduced N (N_{red}) emissions coming predominantly from intensive animal units or large animal colonies, and oxidised N (N_{ox}) emissions coming from energy combustion,

so that preventative legislation may need to be targeted; (2) spatially the different N forms tend to originate and deposit in different places so that the likelihood, risk, of the different forms affecting greenhouse gas (GHG) release from bogs will be affected by the surrounding land use and terrain: ammonia (NH_3) is a highly reactive, alkaline gas that deposits close, within 1 to 2 km of the source, whereas NO_3^- and ammonium (NH_4^+) in wet deposition are deposited remotely and affected by rainfall amount, which can be orographically enhanced. Given there are no indications of global N emissions falling, especially with respect to reduced N (Galloway et al., 1998,) there is a pressing need for an *in situ* comparative study of the effects of the different N forms.

This paper reports measurements made between 5 and 9 yr of N additions, as dry NH_3 gas, wet reduced NH_4^+ or wet oxidised NO_3^- , to quantify effects of N on cover of key components of the vegetation, N availability and losses as the GHG, N_2O . The bog vegetation is typical of peatlands dominated by hummocks supporting dwarf ericaceous shrubs and hummock-forming *Sphagnum*. The automated experiment provides a unique simulation of real-time N deposition, the doses, frequency (> 100 spray events yr^{-1}) and exposure concentrations (4 mM) reflecting the pollution climate experienced in the UK. Ambient N inputs are relatively low, so that the responses should be indicative of the likely potential impacts of anthropogenic N inputs on more pristine northern European peat bogs. In previous pollution effects studies where N pollution was confounded with that of sulphur and sites had been severely polluted for decades (Press et al., 1986), it was difficult to establish what effects, particularly with respect to the loss of sensitive species, had already taken place and to what extent the system was already primed with N.

The vegetation responses in permanent quadrats to different loads of reduced N as NH_3 or NH_4^+ were reported in detail for the sampling period 2002–2009 (Sheppard et al., 2011). That paper demonstrated conclusively that NH_3 reduces the cover of sensitive species at much lower N doses than NH_4^+ and that the threshold concentration for detrimental effects decreases with the length of exposure. Photographs of the visible damage associated with the reductions in cover, and the interactions with biotic and abiotic stress are described there and in Sheppard et al. (2008). In this paper we examine links between species change, dry deposited NH_3 and wet deposited NH_4^+ and NO_3^- , and biogeochemical cycling, based on the whole plot vegetation cover after 7 yr of N inputs.

1.1 Aims

This paper has two aims:

- to determine the effects of elevated N deposition as NH_3 , NH_4^+ or NO_3^- under “real world” conditions, on

peatland vegetation cover and its ability to immobilise the incoming N.

- to determine the fate of N in above-ground vegetation, soil water, peat and as N_2O emissions and show whether the form of N influences the amount of N in the various components.

1.2 Hypothesis

If N is limiting, enhanced N deposition should stimulate vegetation growth, depending on P availability and increase the N immobilization capacity of an ombrotrophic peatland, maintaining a low soil water N concentration and minimising losses as N_2O .

2 Methods

2.1 Site

Whim bog in the Scottish Borders (282 m a.s.l., $3^{\circ}16' \text{W}$, $55^{\circ}46' \text{N}$) represents a transition between a lowland raised bog and blanket bog, on 3–6 m of deep peat. Mean air and soil (10 cm depth) temperature (2003–2009) were 8.6°C (-9.2°C to 27.7°C) and 7.7°C respectively. The mean relative humidity and annual rainfall were 89 % and 1092 mm (734–1462 mm) respectively. Continuous water table measurements at the site since 2003 indicate means of 24, (drought year 2003), 12, 12, 9, 5, 10, 6 cm up to 2010, measured as cm below the peat surface, i.e. relatively wet for most of the year. Ambient N deposition (wet + dry) is $\sim 8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Sheppard et al., 2004). The peat is very acidic, with pH ~ 3.4 (3.27–3.91 in water). The vegetation is classified as a *Calluna vulgaris*–*Eriophorum vaginatum* blanket mire community UK NVC M19 (Rodwell, 1991). Replicate plots are highly variable and dominated by unmanaged *Calluna* of variable age and stature occurring as mosaics containing *Calluna* and *Sphagnum capillifolium* hummocks and hollows containing *S. fallax* and *S. papillosum*. Other common species include *Erica tetralix* and the mosses *Hypnum jutlandicum* and *Pleurozium schreberi*. The main species identified above are herein referred to by their genera, e.g. *Calluna*, *Sphagnum*, *Eriophorum*, *Erica*, *Hypnum* and *Pleurozium*.

2.2 Treatments

N is added in wet deposition at three target doses, but only the seven times ambient deposition (equivalent to $56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) and the control (no added N) have been evaluated in this study. Nox is added as NaNO_3 and Nred as NH_4Cl , designated Nox56 and Nred56, respectively, at a concentration of 4.0 mM. Treatments, made up from concentrated solutions diluted in rainwater, are transferred to each plot via 100 m lengths of 16 mm pipe, terminating in a central sprayer with a spinning disc that uniformly distributes

the treatment to the 12.8 m^2 plot. Each treatment is replicated once within each of 4 blocks (i.e. 4 replicate plots per treatment), including 4 control plots that receive the additional precipitation ($\sim 10\%$) but no treatment N. Plots are treated automatically when sufficient rain water has been collected and when air temperature exceeds 0°C and wind speed is $< 5 \text{ m s}^{-1}$ (Sheppard et al., 2004, 2011).

A dry deposition treatment approximating to the wet N deposition was included in the comparison. An exponential gradient of NH_3 concentrations is achieved via free air release: NH_3 is supplied from a cylinder of pure compressed liquid NH_3 , diluted with ambient air and released from a perforated 10 m pipe, 1 m off the ground when the wind direction is between 180 – 215° , temperatures exceed freezing and wind speed exceeds 2.5 m s^{-1} (Leith et al., 2004; Sheppard et al., 2011). In this study, samples and sampling were undertaken 8 m from the NH_3 source, which receives between 56 – $68 \text{ kg NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$, depending on wind direction. A full description of how measured NH_3 concentrations are converted to $\text{NH}_3\text{-N}$ deposition can be found in Sheppard et al. (2011).

Meteorological variables for wind direction, wind speed, solar radiation, rainfall, surface wetness, mean air temperature, soil temperature (10 and 20 cm) and water table height at the site are recorded, as 1- or 15-min averages (Leith et al., 2004).

2.3 Assessments of cover, biomass and N concentrations in the most abundant species

The fate of the applied N was estimated in August 2009 from the percentage cover of the 12.8 m^2 plots occupied by the common species. *Calluna* was destructively sampled (one stem including the buried part) at 24 standardized points approximating to a known area for each plot. This provided an unbiased representation of the different ages of *Calluna*. Each stem was measured along with the length that supported green foliage. The green foliage was removed from the wood and each was dried, weighed and ground for CN analysis. Standing, above-ground *Calluna* biomass was extrapolated to g m^{-2} from the % cover and weight per harvested area. The proportion of wood to green and the N concentration in each was used to derive the weight of N immobilized in the foliage and wood compartments.

Litter production was measured between 2007 and 2009, together with seasonal changes in the chemistry (2007/2008), and upscaled (g m^{-2}) based on changes in cover in permanent quadrats. Three wire mesh collecting trays, providing 108 cm^2 per plot or distance along the NH_3 transect, were placed under *Calluna* and emptied seasonally, the contents cleaned of vole excrement, dried at 80°C for 5 days, weighed and ground for CN analysis, using a CN analyser. Annual mean data based on the individual seasons are presented.

Three clumps of *Eriophorum* were randomly harvested from each plot, the area measured by placing a wire grid

over the top and the biomass separated into green leaves, leaf bases and roots, dried, weighed and ground for CN analysis. Of the *Sphagnum* species, only *S. capillifolium* was assessed, as the other species generally formed < 1 % of the cover. The average depths of the hummocks (patches in each plot) were estimated by inserting a cane into each hummock until resistance was met. Destructive harvests outside the plots were used to convert depth into a weight per known area, which was upscaled to g m⁻² from plot cover values. The N concentration was measured in both the capitulum and the “brown” stems. The relative weights of capitulum and stem were estimated from 10 destructive harvests off plot for a range of hummock depths, and this was used together with the respective % N to estimate the g N m⁻². Biomass of *Hypnum* and *Pleurozium* was estimated from their respective growth through plastic netting (10 × 15 cm, 3 × 3 mm square holes) placed over each moss in March 2008, pegged down and removed in April 2009. The annual growth, estimates of the depth of moss and cover in each plot, together with C and N chemistry, were used to calculate the nutrient store in the green and senescent moss.

Cover and sampling along the NH₃ transect was measured in two 2 × 1 m quadrats positioned parallel to the release pipes, one on either side of the central board walk that divides the transect. Sample values represent the mean of these two sampling points where 4 subsamples were bulked to provide the sample for analysis.

2.4 Soil water mineral N concentrations, KCl, extractable mineral N, total N, N₂O fluxes and bulk density (BD)

Since 2006, mini rhizon suction samplers (0.45-μm membrane filter to minimise access from microbes) attached to a 60 mL syringe have been in place 0–10 cm below the peat surface, predominantly under hypnaceous mosses, one per plot, sampling soil water and emptied every 28 to 35 days, monthly. These syringes were covered with a large turf of peat to exclude the light and keep them cool. Concentrations of soil water NO₃⁻ and NH₄⁺ were measured by ion chromatography following filtration. The detection limits were 0.062 and 0.014 mg L⁻¹ for NO₃-N and NH₄-N respectively. In November 2009 two samples per plot of the top 10 cm of soil were removed below the senescent vegetation, bulked, dried at 105 °C, ground (ball mill) and analysed for N, (CN analyser). Subsamples were extracted in M KCl in 1 : 5 ratio, shaken for 1 h, filtered, (Whatman 42 filter paper) and mineral N measured using an auto-analyser. BD cores, one per plot, were removed from beneath shallow layers of hypnaceous moss, to a depth of 30 cm, using a peat BD corer, separated into 10 cm layers, dried at 110 °C and weighed. Adjustments, based on measurements of the depth of the hole, were made for compression and 0 cm represented the point at which the humified black brown peat was visible.

GHG measurements were made using closed (non-steady state) static chambers (40 cm diameter × 20 cm height) with an opaque lid. In 2006, chambers were firmly inserted into each of the four treatment plots, one per plot, to different depths depending on the unevenness of the ground surface. Volumes were estimated by placing a ruler at 15 different points inside the box to measure the depth to the vegetation and taking the average height to estimate the volume of the box. Dipwells to measure the water table, 70-cm plastic pipes of 4-cm diameter, perforated with 4-mm holes every 5 cm down both sides and fitted with a top end cap, were installed adjacent to each chamber. Water table depth was measured simultaneously with trace gas sampling, and soil temperature was taken from the site measurements. N₂O was measured on approximately 8–10 occasions in both 2010 and 2011 between April and October. The chambers were enclosed for up to 40 min and four air samples removed from the headspace after mixing the air using the syringe for analysis into 20 mL glass vials using the double needle approach, passing 100 mL through the vial. Vials were stored for a maximum of 5 days before N₂O was measured by electron capture detector (ECD) gas chromatography. The oven was operated at 50 °C and the ECD at 350 °C. Certified N₂O standards were included at the start and end and between every 10 samples. Data, four concentrations over 40 min, were tested for non-linearity, and analysed by linear regression or by fitting a curved response (Pedersen et al., 2010). Some data points (10–15 %) were rejected when the change in the chamber gas concentration failed to fit either of these models; the remainder were used to calculate the N₂O flux, rate of change in N₂O concentration over time.

2.5 Statistical analysis

Data (% N, cover and biomass) were tested for normality and homogeneity of variance (GenStat 12). A one way generalised model, without blocking, was used to separate the effects of N form with post hoc tests (Tukey) where justified, using GenStat 12 (GenStat 12).

3 Results

3.1 Species cover

There were no significant ($p = 0.807$) effects of high N among the wet N treatments, but dry NH₃ significantly ($p < 0.001$) reduced (eliminated) *Calluna* cover (Fig. 1). *Eriophorum* cover did not differ significantly ($p = 0.546$) between the treatments. Cover of the common non-vascular plants (*S. capillifolium*, *H. jutlandicum* and *P. schreberi*) was also eliminated by the NH₃ treatment, while *H. jutlandicum* and *P. schreberi* were also significantly affected ($p = 0.015$ and $p < 0.001$ respectively) by the high wet N treatments. Both Nox and Nred significantly reduced the cover of *Pleurozium*, whereas Nox increased the cover of *Hypnum* while

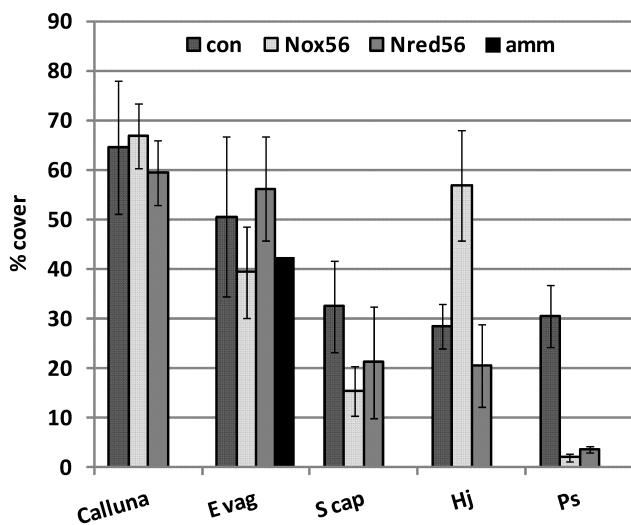


Fig. 1. Percentage cover of the main species *Calluna*, *Eriophorum vaginatum* (Evag), *Sphagnum capillifolium* (Scap), *Hypnum jutlandicum* (Hj) and *Pleurozium schreberi* (Ps) (+/- sterr) growing in the 12.8 m² plots on the control (no added N) and N treated (oxidised (Nox), reduced (Nred) and ammonia (amm)) plots (~56 kg N ha⁻¹ yr⁻¹) at Whim bog in 2009. Note that the mosses and *Calluna* have gone from the NH₃ plots.

Nred reduced it, though not significantly (Fig. 1). Fifty percent of the ground along the NH₃ transect was bare, compared to < 1 % in the wet treatments.

3.2 %N

Among the component species of this bog vegetation, the green leaves of the graminoid *E. vaginatum* have the highest % N, with mosses, ericoid shoots, litter, decaying vegetation and peat having similar but almost 50 % lower N concentrations. Woody material and leaf bases have the lowest N concentrations (Fig. 2). N concentrations were significantly ($p < 0.05$) increased by the addition of 56 kg N ha⁻¹ yr⁻¹. In *Calluna* wet and dry Nred treatments significantly increased % N compared to Nox in wood, litter and green shoots. *S. capillifolium* capitula had significantly more % N with Nred than Nox, whereas in the stem necromass the effect of N form was not significant ($p > 0.05$). The general moss necromass, however, did have significantly ($p < 0.05$) more N with Nred than Nox. In *Hypnum* there was no effect of N form. The only species that survived the high NH₃ treatment, *E. vaginatum*, had significantly ($p < 0.05$) higher N concentrations in its green leaves and leaf bases with NH₃ than with the wet N treatments, which hardly increased % N (Fig. 2).

3.3 Soil water nitrate and ammonium

Annual mean NO₃⁻ concentrations are shown in Fig. 3. Control NO₃⁻ concentrations showed no trend since measurements began in 2006 and averaged 0.3 mg L⁻¹. The wet N

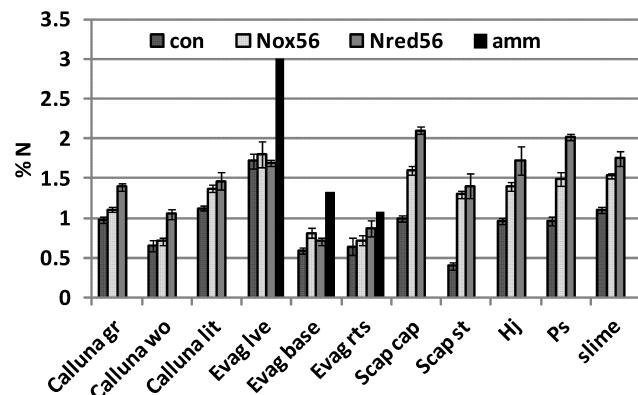


Fig. 2. Percentage of N (dry wt) (+/- sterr) in the main above-ground vegetation on the control (no added N) and N treated (oxidised (Nox), reduced (Nred) and ammonia (amm)) plots (~56 kg N ha⁻¹ yr⁻¹) at Whim bog in 2009: green *Calluna* shoots (*Calluna* gr), *Calluna* woody stems (*Calluna* wo), *Calluna* litter (*Calluna* lit), *Eriophorum vaginatum* green leaves (Evag lve), *E. vaginatum* leaf sheaths (Evag base), *E. vaginatum* surface roots (Evag rts), *Sphagnum capillifolium* capitula (Scap cap), *S. capillifolium* brown stem (Scap st), *Hypnum jutlandicum* (Hj), *Pleurozium schreberi* (Ps) and slime (necrotic senescing hypnaceous moss and fine roots). Values for all but *Evag* are missing for the amm treatment as there was no material to sample.

treatments increased NO₃⁻ concentrations by 5 and 3 times for Nox and Nred respectively. By contrast NH₃ increased NO₃⁻ concentrations by a factor of 50. Similarly for NH₄⁺ the wet N treatments caused 3- and 9-fold increases above 3 mg L⁻¹ for Nox and Nred respectively and a 42-fold increase with NH₃.

3.4 Extractable NO₃⁻ and NH₄⁺, total soil N, bulk density and N₂O fluxes

KCl extractable NH₄⁺, but not NO₃⁻, was significantly ($p < 0.05$) increased with high NH₃, but for NO₃⁻ there were no N treatment effects (Fig. 4). Wet N almost doubled NH₄⁺, but reduced NO₃⁻ concentrations, although these increased with dry N (Fig. 4). The form of the N addition made no difference to the amount of NH₄⁺-N or NO₃⁻-N that was extracted in KCl. Total N in the top 10 cm of peat was not significantly affected by the N additions (Fig. 5). However, there was a strong trend for N additions to increase bulk density especially in response to NH₃ (Fig. 5), which has the effect of making the soil N store much larger. The addition of wet N as NH₄⁺ or NO₃⁻ did not significantly ($p > 0.05$) increase losses of N as N₂O compared with the dry deposition of NH₃ (Fig. 6). N₂O emissions from the wet N treatments, while very low, were generally 2–3 times higher with Nox than Nred, which appeared to suppress denitrification.

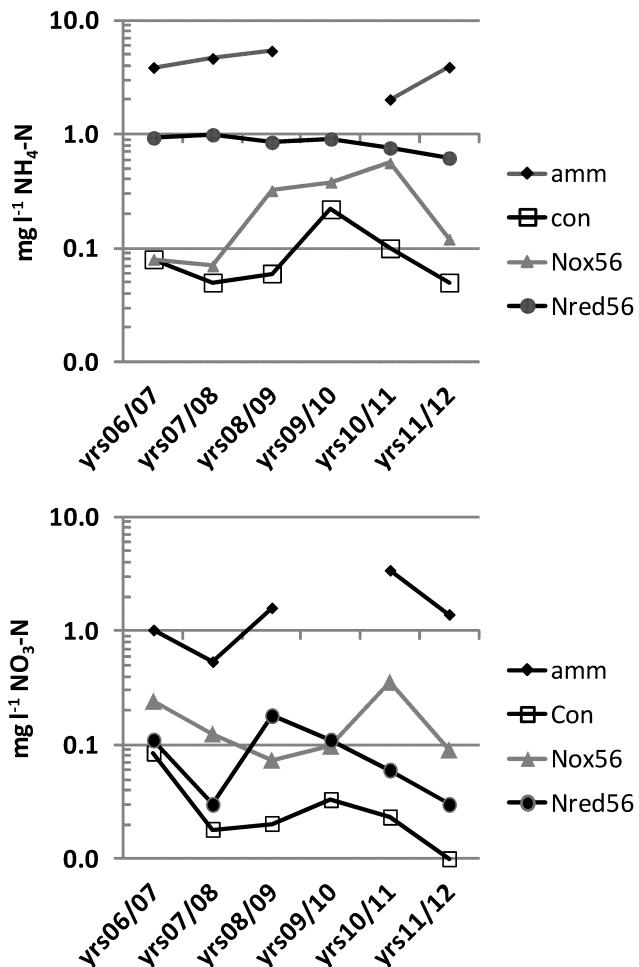


Fig. 3. Annual mean concentrations of nitrate and ammonium N (\pm st err) in soil pore water collected with suction samplers emptied monthly. Data from 2006 for the control (no added N) and N treated (oxidised (Nox), reduced (Nred) and ammonia (amm)) plots ($\sim 56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) at Whim bog. No data were collected for the amm plots in years 2009/2010.

3.5 N sequestered in above-ground vegetation and the peat

Adding N as dry NH_3 doubled the amount of N in the peat pool, whereas increases with wet N, while significant ($p < 0.05$), were smaller. Wet N additions irrespective of form did not significantly enhance the above-ground pool of N in vegetation, and dry deposition almost eliminated this N pool (Fig. 7). In control plots 69 % of the N present was measured in the peat, compared to 75.9 and 75.5 % in the wet N treatment plots and 96.5 % in the dry N plots. Because of the devastating effect of NH_3 on all plants except *Eriophorum*, in this treatment the N was split between the peat and the *Eriophorum*.

In the wet N treatments the proportion of N in *Calluna* litter was doubled from 3.4 to 6.6 or 7 %. The proportion

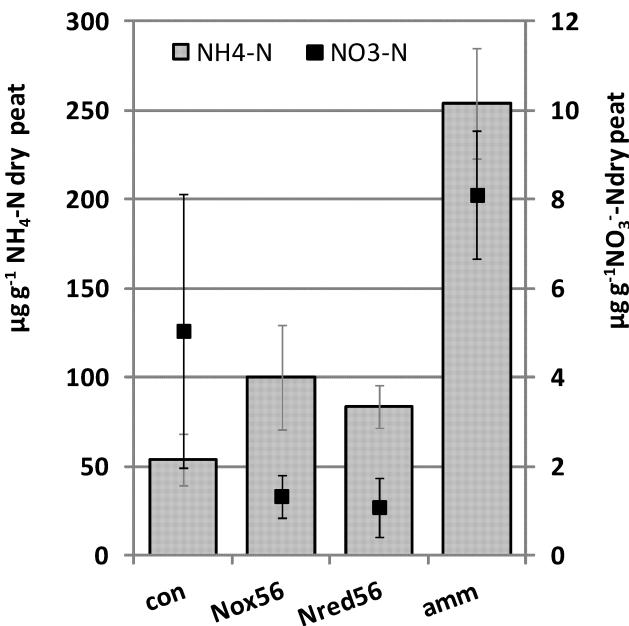


Fig. 4. KCl extractable $\text{NH}_4\text{-N}$ (grey bars) and $\text{NO}_3\text{-N}$ (small black squares) (\pm st err) in the surface 0–10 cm peat from the control (no added N) and N treated (oxidised (Nox), reduced (Nred) and ammonia (amm)) plots ($\sim 56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) at Whim bog in 2009 (November).

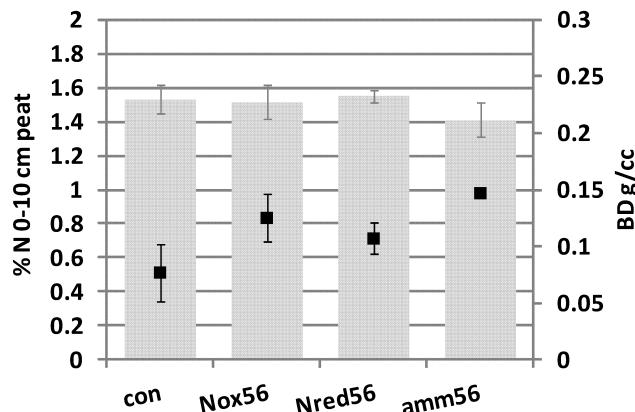


Fig. 5. Percentage of N (dry wt), bars, (\pm st err) in the 0–10 cm peat from the control (no added N) and N treated (oxidised (Nox), reduced (Nred) and ammonia (amm)) plots ($\sim 56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) at Whim bog in 2009 (November) and, on the right-hand axis, the bulk density (BD).

of N in the senescent moss/root layer, 2.7 % (slime), was the same in the control and Nox treatments, but in the Nred treatment only 0.3 % of the N was in this pool. The proportion of N in *Calluna* was not affected by the wet N treatments at 5.4, 5.1 and 6.8 % in the control, Nox and Nred respectively. The proportion of N in *Eriophorum* was similar in all treatments 3.8, 2.8, 2.7 and 3.5 % respectively in the control, Nox, Nred and amm56 treatments respectively. There were bigger

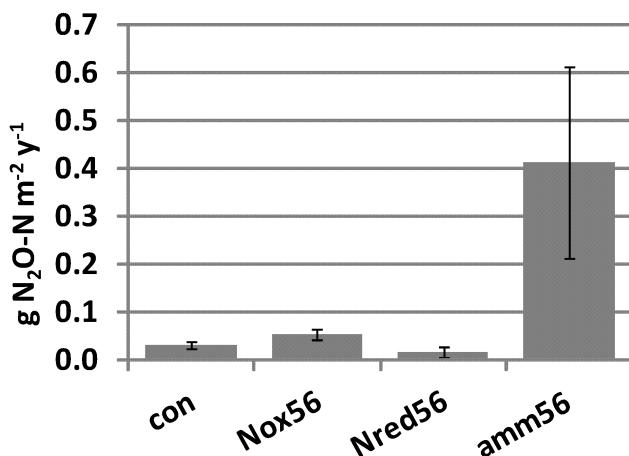


Fig. 6. Mean $\text{N}_2\text{O-N}$ flux (+/– sterr) from the control (no added N) and N treated (oxidised (Nox), reduced (Nred) and ammonia (amm)) plots ($\sim 56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) at Whim bog in 2009 and 2010.

differences in the proportion of N in *Sphagnum capillifolium*. Most, 12.2 %, was in the control but only 4.1 % in the Nox and 7 % in the Nred treatment. N additions, especially Nred, diminished the pool of N in the pleurocarpous mosses from 3.4 % to 2.5 and 0.8 % respectively for Nox and Nred.

4 Discussion

4.1 Does adding N to an ombrotrophic peatland increase biomass and N retention?

Irrespective of the form in which N was applied, $56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ did not enhance vegetation cover. Rather it decreased it, especially when the N was applied as NH_3 . Foliar N concentrations were increased, but without an increase in biomass this represented little N retention. Curtis et al. (2005) concluded that the moss/lichen (cryptogam) layer present in UK moorlands can actively sequester N deposition, but with declining effectiveness with increasing N load, as cryptogam biomass was strongly negatively related to increasing N deposition. Our experimental evidence, based on following species cover and foliar N over time, corroborates the findings of Curtis et al., indicating a decline in retention. The study of Curtis et al. (2005) was based on providing ^{15}N fortnightly for one year to four catchments with ambient N deposition between 6.4 and $30.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and measuring ^{15}N in the harvested biomass. We have compared N in harvested vegetation and species cover for no N input (control) versus $56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. Like Curtis et al. (2005) we have direct evidence of the link between N effects on above-ground vegetation and the inability of the system to retain N, measuring increased NO_3^- in the soil water, and also higher N_2O fluxes. N_2O emissions and concentrations of soil water NO_3^- concentrations for 2008/2009, not reported here, were

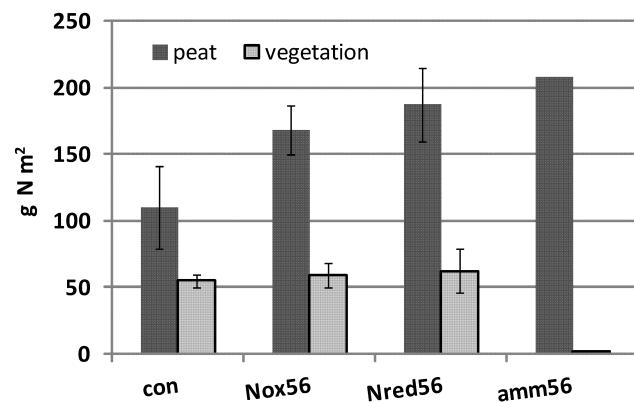


Fig. 7. Immobilization of N above and below ground, in the peat from the control (no added N) and N treated (oxidised (Nox), reduced (Nred) and ammonia (amm)) plots ($\sim 56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) at Whim bog in 2009.

particularly high, coinciding with the lowest vegetation cover on the NH_3 transect, before the *E. vaginatum* cover had increased.

One reason why N has not been effectively retained at Whim bog could be linked to P availability. The availability of N is not the only nutrient that can affect growth in semi-natural systems; at Whim, phosphorus (P) availability and possibly potassium (K) influenced the N response, at least in the early years (Carfrae et al., 2007). When P/K was added in a 1 : 14 ratio of N : P, there was indirect evidence of an improvement in *Sphagnum* growth and a reduction in % N. Measurement of shoot elongation and % N in 2008 (Kivimaki, 2011) indicated the P/K effects on *S. capillifolium* were sustainable, but there was no interaction with N form. As found in previous studies, co-limitation by P/K will reduce the effectiveness of *Sphagnum* (Breeuwer et al., 2009) and other species present (e.g. *Calluna*) to retain N (Pilkington et al., 2007).

4.2 How does the vegetation respond to N?

In this study we have realistically modified N deposition to a peatland and compared the effects of dry and wet deposition and within wet deposition, Nred and Nox on the fate of the added N. The N dose used here was less than twice the highest UK values, $> 25 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in the Peak District, but up to 6 times the deposition to peatlands in the cleanest N deposition areas between 8 and $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (CBED, 2006–8; see Smith et al., 2000 and Smith and Fowler, 2001 for detail on estimating concentration based deposition). These higher N doses substitute for time, in theory compressing the length of time needed to detect effects (ROTAP, 2011).

The N dose applied ($56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$), especially as NH_3 , significantly decreased moss biomass, *S. capillifolium* and *P. schreberi*, confirming the adverse effects of N on both these mosses (Solga et al., 2005; Salemaa et al., 2008

(*Pleurozium*); Carfrae et al., 2007 (*S. capillifolium*); Lamers et al., 2000 (*Sphagnum* species)). Within 2 yr NH₃ had killed all the *S. capillifolium*, although in the wet Nox and wet Nred plots cover was only reduced by ~30 or ~50 % respectively. These high N doses significantly increased the N concentration, by >30 %, arguably contributing to the N-induced toxic effects on these two mosses and their ultimate demise (Sheppard et al., 2011). Semi-natural ecosystems that have evolved under conditions of low N availability mostly contain plant species that use nutrients conservatively (Aerts, 1999). Such plant species generally have a finite capacity to use N and a limited ability to control uptake making them sensitive to accumulation of potentially toxic NH₄⁺ ions (Sheppard et al., 2011). Mechanisms behind NH₄⁺ toxicity are described in detail by Krupa (2003) and at the cellular level revolve around cell membranes. Ammonium ions function as an electron acceptor, enabling them to uncouple electron transport along membranes and also attack membrane lipids, disabling their functionality. For these sensitive mosses even the lower N dose of 8 kg N ha⁻¹ yr⁻¹ (not reported here) failed to stimulate an increase in cover.

Not all components of ombrotrophic peatlands are as sensitive to N load as these mosses. However, generalising over which species will benefit from increased N availability and contribute to the N retention capacity is problematic and can depend on the form of N. Kool and Heijmans (2009) and Bubier et al. (2007) report that dwarf shrubs appear to benefit most from enhanced N availability. Ericoid species make up the dwarf shrub cover at Whim, and none appeared to benefit in the long term from the additional reactive N. The *Calluna* is unmanaged and mostly mature or degenerate, and this could be restricting its ability to respond to N. There was some increase in growth/cover, particularly evident from the increase in litter cover in permanent quadrats over the years in the Nred plots, (Sheppard et al., 2011), but it only reached significance once. Co-limitation by P availability may also be contributing to *Callunas*' muted N response. In the presence of P/K, shoot extension was significantly albeit only by 7 % increased, although not in every year. Rowe et al. (2008) showed that N deposition led to higher phosphatase activity and thus could improve the P supply and acquisition. We measured increased surface phosphatase activity in *S. capillifolium* and *H. jutlandicum*, in proportion to their N concentration (Phuyal et al., 2007).

At Whim, *Calluna* constrains *E. vaginatum* cover (cf. Kool and Heijmans, 2009), who grew both species together for 14 weeks in hydroponics. They suggested that "the ericoids have a higher phenotypic plasticity than the graminoids, and are therefore able to adapt more quickly to the higher nutrient availability". Our long-term field observations generally support this view, but highlight also the role of additional drivers, cf. the Netherlands, where *Calluna* dominance gave way to graminoids following disruption of the canopy by heather beetle/winter desiccation (Heil and Diemont, 1983).

At Whim *Calluna* cover was not significantly changed by the wet N additions, but exposure to NH₃ in conjunction with secondary stress eliminated it (Sheppard et al., 2008), which enabled *E. vaginatum* cover to significantly increase.

Wiedermann et al. (2007) and Nilsson and Eriksson (2011) reported significant changes in vegetation composition on a *Sphagnum*-dominated boreal mire after 5 yr, in response to N additions (30 kg N ha⁻¹ yr⁻¹ as NH₄NO₃). *Sphagnum* cover was decreased, 100 % down to 41 %, concomitantly with an increase in *E. vaginatum* cover from 30 to 70 %, which shaded out the *Sphagnum*. The dwarf shrubs *Vaccinium oxyccoccus* and *Andromeda polifolia* also increased. However, their growth forms are unlikely to compete with *E. vaginatum*. *E. vaginatum* is very well adapted to low N availability, its adaptation representing a trade-off between survival, growth and reproduction (McGraw and Chapin, 1989). At Whim wet N deposition of both Nox and Nred failed to increase *E. vaginatum* cover or N concentration, whereas NH₃ increased both, although growth per se was not measured. N effects on *E. vaginatum* cover would appear to depend on the species composition of its neighbours and their response to N.

Our observations (see also Sheppard et al. (2011) and those of Curtis et al. (2005)) confirm that peatland/moorland vegetation, especially when co-limited by P/K availability, has a finite, relatively small capacity in relation to ambient deposition, to retain reactive N deposition. As a consequence, once deposition exceeds 10–16 kg N ha⁻¹ yr⁻¹, retention of this N by the vegetation will cease. Although N concentrations in *Calluna* litter suggest that the litter layer can contribute to N retention, especially of NO₃⁻ (Edwards et al., 1985), according to Black et al. (1993), peats in particular, but also moorlands, are the least likely semi-natural ecosystems to retain N.

4.3 Immobilisation of N in the peat and N₂O emissions depend on the form of N

At Whim leakage of N as the greenhouse gas N₂O depended on the form in which N was deposited. In response to high NH₃ concentrations/deposition, the vegetation changed dramatically, leading to a domino effect: *Calluna* was killed along with *S. capillifolium*, hypnaceous mosses and *Cladonia* spp. so that for a couple of years the peat was exposed before *E. vaginatum* expanded to revegetate the area. This meant the floristic N sink was much smaller; as a result, both KCl extractable NH₄⁺ and concentrations of soil water NO₃⁻ were significantly elevated. The higher pH associated with NH₃ deposition probably enabled greater nitrification rates. By comparison 8 yr of wet N inputs as Nox or especially Nred barely increased soil water NO₃⁻ concentrations. Despite significant reductions in moss cover, these changes did not lead to exposed peat, cf. NH₃ (Sheppard et al., 2011), probably because of the significant increase in *Calluna* litter

and necrotic moss layer (Sheppard et al., 2011) with relatively high retention capacities.

The enhancement of N_2O fluxes, however, do not just rely on changes in the vegetation sink: Lund et al. (2009) examined the effect of $40 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ applied as NH_4NO_3 in rainwater three times a year for 2 yr to two bogs dominated by similar vegetation to Whim bog. In the absence of N-driven changes in vegetation, they concluded that the N_2O emissions (average $0.07 \text{ g N}_2\text{O-N m}^2$), similar to those measured in the Nox plots at Whim, were initiated through biochemical and microbial responses to N fertilization. According to Moore (1994) peatland N_2O emissions will greatly increase if the microbial cycle starts to leak, once nitrification and thus denitrification cycles are stimulated, because environmental conditions in bogs generally favour N_2O production. Our observations indicate a strong relationship between soil water NO_3^- concentrations and denitrification, in keeping with the idea of a NO_3^- concentration threshold for denitrification (Henrich and Haselwandter, 1997). In the Nox plots it appears that even NO_3^- additions have so far been insufficient to raise NO_3^- concentrations and upregulate denitrification (Henrich and Haselwandter, 1997). At Whim the lowest N_2O fluxes were measured in the Nred plots, not the controls, which received no treatment N and had the smallest soil water NO_3^- concentrations, suggesting that the high NH_4^+ concentrations may suppress denitrification.

Values for N_2O emissions from Whim bog are based on 2 yr of monthly data collected between May and November and do not represent annual cycles. The low values are, however, broadly similar to other peatland emission values, e.g. Hudson Bay lowland, (Schiller and Hastie, 1994) and W Ontario, (Urban and Eisenreich, 1988), with the exception of the NH_3 treatment, which increased emissions 100 fold. We suggest that peatlands need to undergo a significant N driven perturbation before they are likely to contribute to global N_2O emissions. There was substantial N enrichment with wet N, but because these N forms have not so far significantly changed vegetation composition the domino response has not been set in motion and thus N_2O losses have remained small. In 2008/2009 both N_2O fluxes and soil water NO_3^- concentrations in response to NH_3 were much higher than reported here for 2010/2011, coinciding with the minimum cover of live vegetation, but while the mosses and *Calluna* were senescing, and potentially releasing labile carbon.

Dise and Verry (2001) reported no effects of $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ additions as NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ to a Minnesota peat bog on N_2O , either emission or uptake. Nykanen et al. (2002) recorded negligible fluxes in response to $100 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, except for the odd measurable flux, in a 5-yr study. A review of N enrichment effects on GHG emissions (Liu and Greave, 2009) found that N_2O emissions depended on the form of N ($p < 0.05$), dose ($p < 0.01$) and length of experiment, i.e. cumulative N load. N_2O emissions were mostly negligible until annual additions exceeded 55

and went up to $150 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. This is consistent with our results, emphasising the importance of N form: even after 8 yr of 56 kg N additions over the background of circa $8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, N_2O emissions were mostly negligible in the wet N treatments, except for the occasional high flux (cf. Nykanen et al., 2002). The emission from wet Nox was however, within the IPCC range of 1 % re-emission of deposited N (IPCC, 2006). The addition of $56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ as dry NH_3 significantly increased N_2O emissions from this bog, such that $4 \text{ kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ were lost, 14 % of the annual addition.

In summary we have shown that a substantial increase ($\sim 8^*$ ambient, over 9 yr $\sim 600 \text{ kg N ha}^{-1}$) in N deposition to an acidic (pH 3.6–3.8) peatland can substantially increase the GHG N_2O emissions by > 100 fold, but this only occurs when the vegetative sink is compromised. When the peatland plant community remains intact and vital, the additional N appears to remain in the peat and vegetation (Fig. 7) with negligible leakage. In this study the accumulation of N in the peat partly reflects the increase in bulk density, a consequence of the loss of easily decomposed material at the surface leading to a compression of the peat (Johnson et al., 1990). Increases in % N in the peat were quite variable across treatment plots. A much larger more extensive sampling of the plots, which takes account of the different proportions of plant functional groups, would be required to detect significant changes in peat N.

The causes underpinning differences in N_2O emissions related to N form are not fully established, but we have suggested several reasons why dry deposited NH_3 significantly increased N_2O emissions compared with wet N deposition as Nox or Nred. The addition of N as NH_3 significantly changed the composition of the vegetation (Sheppard et al., 2011) and in doing so reduced the vegetation cover on the peat exposing circa 30 %, which has subsequently been colonised by an expansion of *E. vaginatum* and a different, more nitrophilic bryophyte community. We suggest therefore that, in accordance with the highly significant increase in soil water NO_3^- , reflecting the reduction in the vegetation N sink, more was available for denitrification. This pathway for N loss was further enhanced by the significant 0.5–1 unit increase in soil pH that has been measured (unpublished data), taking the pH from 3.8 sometimes up to 4.8, greatly improving conditions for nitrification of NH_4^+ (Nicol et al., 2008).

Thus, on this ombrotrophic peatland the fate of the reactive N deposition strongly depended on the form of the N deposition, since for the same dose reduced N has caused very different responses depending on whether it was deposited dry or wet, whereas the differences between wet Nred and wet Nox were not significant. If the N is deposited wet, then our observations indicate most of the N can, in the short-term, be retained within the system, despite the modest capability of the vegetation to retain the N. While the peatland plant community maintains its shrubs and moss, *Sphagnum* understorey, almost all the N is retained by the soil. Our

N inputs are on the low side by comparison with the loads needed to stimulate N₂O emissions (Liu and Greaver, 2009), but they highlight the importance of the vegetation response, and the extent to which it is co-limited by P/K, in determining whether anthropogenic N deposition will be retained or leak from peatlands. These observations support the N cascade theory (Galloway et al., 2003): once the second threshold has been exceeded (i.e. N is no longer limiting and biological retention has been rendered ineffective through saturation with toxic NH₄⁺ ions), in imperfectly drained soils with sufficient labile organic C, N can leak out as N₂O or leach as NO₃⁻.

5 Conclusions and implications

Results from this 10-yr study show that when ombrotrophic peatlands, dominated by hummock-forming *Sphagnum* species, are exposed to N as NH₃, the effects are mostly detrimental, because NH₃ is toxic to this keystone moss and other hypnaceous mosses that contribute to N immobilisation. Depending on the level of N deposition, rapid disruption of the vegetation can occur, causing exposure of the peat and opening up of the N cycle leading to N losses as the GHG N₂O. GHG emissions as methane (CH₄) may also be increased since *Eriophorum vaginatum*, a sedge that takes over on the bare peat, provides a conduit for CH₄ that bypasses the aerobic zone. Wet N deposition takes much longer to have a negative impact on *Sphagnum* cover and is less detrimental to the overall canopy structure so that more N is immobilised and very little lost as N₂O. Even after 10 yr of 56 kg N ha⁻¹ yr⁻¹ inputs, we cannot say with confidence whether wet deposited N will be as degrading over the long term as dry deposition and lead to increased N₂O emissions. However, wet N deposition, irrespective of the form of N, appears to be detrimental to the vitality of *S. capillifolium*, the main peat forming species in this peatland, implying that enhanced N deposition to similar peatlands could ultimately restrict their ability to sequester C.

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