Science of the Total Environment 559 (2016) 113–120

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Sphagnum can 'filter' N deposition, but effects on the plant and pore water depend on the N form

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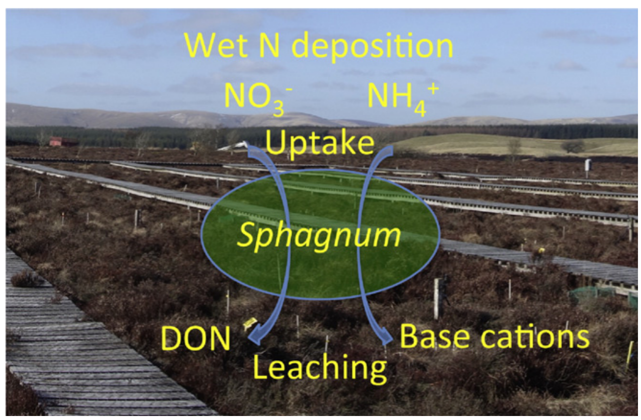
HIGHLIGHTS

- The *Sphagnum* N filter is more resilient to wet N deposition than previously inferred.
- The N filter was more compromised when NH_4^+ dominates wet deposition at high inputs (64 kg N ha^{-1} yr^{-1}).
- The N filter function was reflected in pore water chemistry and the different mechanisms of NH_4^+ and NO_3^- assimilation of *Sphagnum* can explain the effects of wet N form on species change in peatland ecosystems.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 December 2015
Received in revised form 18 March 2016
Accepted 18 March 2016
Available online 5 April 2016

Editor: D. Barcelo

Keywords:
Manipulation experiment
Tissue N
Dissolved organic nitrogen
Base cations
N uptake

ABSTRACT

The ability of *Sphagnum* moss to efficiently intercept atmospheric nitrogen (N) has been assumed to be vulnerable to increased N deposition. However, the proposed critical load (20 kg N ha^{-1} yr^{-1}) to exceed the capacity of the *Sphagnum* N filter has not been confirmed. A long-term (11 years) and realistic N manipulation on Whim bog was used to study the N filter function of *Sphagnum* (*Sphagnum capillifolium*) in response to increased wet N deposition. On this ombrotrophic peatland where ambient deposition was 8 kg N ha^{-1} yr^{-1}, an additional 8, 24, and 56 kg N ha^{-1} yr^{-1} of either ammonium (NH_4^+) or nitrate (NO_3^-) has been applied for 11 years. Nutrient status of *Sphagnum* and pore water quality from the *Sphagnum* layer were assessed. The N filter function of *Sphagnum* was still active up to 32 kg N ha^{-1} yr^{-1} even after 11 years. N saturation of *Sphagnum* and subsequent increases in dissolved inorganic N (DIN) concentration in pore water occurred only for 56 kg N ha^{-1} yr^{-1} of NH_4^+ addition. These results indicate that the *Sphagnum* N filter is more resilient to wet N deposition than previously inferred. However, functionality will be more compromised when NH_4^+ dominates wet deposition for high inputs (56 kg N ha^{-1} yr^{-1}). The N filter function in response to NO_3^- uptake increased the concentration of dissolved organic N (DON) and associated organic anions in pore water. NH_4^+ uptake increased the concentration of base cations and hydrogen ions in pore water though ion exchange. The resilience of the *Sphagnum* N filter can explain the reported small magnitude of species change in the Whim bog ecosystem exposed to wet N deposition. However, changes in the leaching substances, arising from the assimilation of NO_3^- and NH_4^+, may lead to species change.

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http://dx.doi.org/10.1016/j.scitotenv.2016.03.130

1. Introduction

Elevated atmospheric nitrogen (N) deposition and its ecological impact is an issue of widespread concern. Peatlands have a significant impact on the global C cycle and there is estimated to be 500 Pg C stored in northern peatlands (Yu, 2012), one-third of the global surface soil C pool (Gorham, 1991). *Sphagnum* moss plays a central role in peatland sustainability and carbon (C) sequestration. *Sphagnum* species in peatland are described as 'ecosystem engineers' creating acidic, nutrient-poor, and water saturated soils, enabling them to outcompete other plants (Van Breemen, 1995). The impact of elevated atmospheric N deposition on peatland ecosystems is therefore likely to be mediated through effects on *Sphagnum* species.

Understanding how *Sphagnum* removes inorganic N from precipitation and the effects of increasing N inputs on this process is key to predicting N effects on peatland ecosystems. *Sphagnum* mosses are adapted to nutrient-limited conditions (Van Breemen, 1995). Having no rhizoids and internal water-conducting tissue like other non-vascular plants, *Sphagnum* efficiently intercepts nutrients, including N, coming from the atmosphere (Bobbink et al., 1998; Van Breemen, 1995). The efficient N removal by *Sphagnum* has been likened to a filter effect (Lamers et al., 2000). However, there are limits to the capacity of this filter; as atmospheric N deposition increases the *Sphagnum* N filter fails and mineral N levels in the rhizosphere increase (Bragazza et al., 2005; Lamers et al., 2000). The increased N availability in the rhizosphere can promote the growth of vascular plants (Berendse et al., 2001; Bragazza et al., 2012; Heijmans et al., 2001; Limpens et al., 2003). Thus, elevated atmospheric N deposition can lead to species change, changes in decomposition rates and ultimately reduce C accumulation in peatland ecosystems (Berendse et al., 2001; Bragazza et al., 2012; Heijmans et al., 2001; Limpens et al., 2011; Sheppard et al. 2014).

Sphagnum moss has been assumed to be vulnerable to increased N deposition. *Sphagnum* N status across a natural gradient of ambient atmospheric N deposition revealed that elevated atmospheric N deposition increased tissue N concentrations of *Sphagnum* (*e.g.* Malmer and Wallén, 2005; Pitcairn et al., 1995; Wiedermann et al., 2009) leading eventually to N saturation of *Sphagnum* (Bragazza et al., 2004; Bragazza et al., 2005; Limpens et al., 2011; Lamers et al., 2000; Harmens et al., 2014). The critical load causing N saturation of *Sphagnum* with increased N availability in the rhizosphere has been proposed at 20 kg N ha^{-1} yr^{-1} (Harmens et al., 2014; Lamers et al., 2000). However, the proposed critical load of N deposition to exceed the capacity of the *Sphagnum* N filter has not been confirmed.

Long-term and realistic *in situ* manipulation studies are urgently needed to elucidate the above question. However, few such studies have been conducted at the proposed critical N load (20 kg N ha^{-1} yr^{-1}) and below except for those by Granath et al. (2009) and Xing et al. (2010). In many N manipulation studies, the N concentration of *Sphagnum* moss exposed to 30–50 kg N ha^{-1} yr^{-1} of N addition increases to 15–20 mg g^{-1} for short-term (2–3 years, Berendse et al., 2001; Fritz et al., 2012; Nordbakken et al., 2003; Tomassen et al., 2003) and long-term (12 years, Granath et al., 2009) experiments, and often greatly exceeds 20 mg g^{-1} (Heijmans et al., 2001). N addition (40–80 kg N ha^{-1} yr^{-1} for up to 4 years) also increased mineral N concentrations in pore water (Limpens et al., 2003; Limpens et al., 2004; Limpens & Berendse, 2003). However, many manipulation studies in peatland have conducted short-term, high N dose experiments that do not simulate the effect of long-term elevated N deposition on peatland ecosystems and thus are unable to assess the *Sphagnum* N filter function in response to increased N deposition. It is likely that the *Sphagnum* N filter function may be vulnerable to acute increases in N availability caused by low frequency N applications at high concentrations that compromise it in a way that frequent small inputs do not.

Since N deposition contains two forms of mineral N in varying proportions (Stevens et al., 2011), we also need to understand the respective effects of reduced (NH_4^+) *versus* oxidized (NO_3^-) N on the N status of the *Sphagnum* moss and the *Sphagnum* N filter function. NH_4^+ is more detrimental to *Sphagnum* than NO_3^- (Manninen et al., 2011; Sheppard et al., 2014), possibly due to the greater toxicity of NH_4^+ (Gerendás et al., 1997; Krupa, 2003; Stevens et al., 2011; Limpens and Berendse, 2003) coupled to preferential uptake of NH_4^+ by *Sphagnum* (Fritz et al., 2014; Liu et al., 2013; Wiedermann et al., 2009). For example, Manninen et al. (2011) found that NH_4^+ addition increased shoot N concentration of *Sphagnum* and decreased photosynthetic variables (F_v/F_m) and shoot dry weight of *Sphagnum*.

Pore water that has passed through the *Sphagnum* filter may differ in terms of water quality including pH (Manninen et al., 2011; Sheppard et al., 2014) when *Sphagnum* is exposed to NH_4^+ and NO_3^- separately. This could be caused by the different exchange processes of *Sphagnum* with respect to N assimilation between NH_4^+ and NO_3^-. In higher plants, NH_4^+ uptake is usually accompanied by cation leaching (Krupa, 2003; Li et al., 2013; Staelens et al., 2008; Stevens et al., 2011) and hydrogen ion (H^+) leaching (Krupa, 2003; Liu et al., 2013; Manninen et al., 2011; Paulissen et al., 2004; Stevens et al., 2011; Tomassen et al., 2003). In contrast, NO_3^- uptake is accompanied by hydroxyl ion (OH^-) loss generated by nitrate reduction (Manninen et al., 2011; Stevens et al., 2011). However, few manipulation studies have evaluated the form of reactive N in wet deposition (Blodau et al., 2006; Paulissen et al., 2004; Sheppard et al., 2014; Sheppard et al., 2013; Van den Berg et al., 2008).

Sheppard et al. (2014) found that 9 years of these treatments significantly reduced the cover of *Sphagnum*, but that the magnitude of change was small, especially at N loads below 32 kg N ha^{-1} yr^{-1} (N additions of 24 kg N ha^{-1} yr^{-1} plus ambient N deposition of 8 kg N ha^{-1} yr^{-1}). They concluded that *Sphagnum capillifolium* is relatively resilient to wet N deposition. In addition, Sheppard et al. (2014) showed that although the magnitude of change is small, the effects of wet N deposition on species change on the peatland were different depending on the N form. We suggest the reasons for this may be due to different interactions between *Sphagnum* and N form resulting from NH_4^+ and NO_3^- assimilation.

This study addresses these gaps in our understanding, assessing the *Sphagnum* N filter function in response to increased wet N deposition supplied separately as NH_4^+ or NO_3^-. The specific objectives were as follows: 1) to assess the *Sphagnum* N filter function in response to 11 years of increased wet deposition, including the proposed critical load of N deposition (20 kg N ha^{-1} yr^{-1}), 2) to evaluate the sensitivity of the *Sphagnum* filter function to different N forms, NO_3^- and NH_4^+, and 3) to evaluate the quality of pore water, including pH and base cations, that has passed through the *Sphagnum* filter. These objectives were addressed using the ongoing N manipulation experiment, established in 2002 on Whim bog in SE Scotland: 8, 24, and 56 kg N ha^{-1} yr^{-1} of wet NH_4^+ (as NH_4Cl) and wet NO_3^- (as $NaNO_3$) has been sprayed separately on each plot of peatland for more than a decade. The experiment has been conducted under 'real' world conditions, where N additions were automated and coupled to rainfall, facilitating frequent small N inputs at concentrations more closely resembling those in wet deposition (Sheppard et al., 2004; Sheppard et al., 2014).

2. Materials and methods

2.1. Study site

The study was conducted at Whim bog (282 m a.s.l., 3°16′W, 55° 46′ N) on 3–6 m of deep peat in the Scottish Borders, 30 km south of Edinburgh, Scotland. No active management has been conducted for at least 70 years. The most common species on this bog, *Calluna vulgaris*, *Eriophorum vaginatum*, *S. capillifolium*, *Hypnum jutlandicum*, *Pleurozium schreberi* and *Cladonia portentosa* occur widely on similar habitats through the northern hemisphere (Gore, 1983). *S. capillifolium* is a hummock forming species. Mean annual air temperature and annual