

Dissolved organic nitrogen dominates in European bogs under increasing atmospheric N deposition

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[1] To assess the effects of increased atmospheric N input on N availability in ombrotrophic peatlands, the relative concentrations of dissolved organic nitrogen (DON) to dissolved inorganic nitrogen (DIN) were measured in bog waters along a natural gradient of atmospheric N deposition. Six European bogs were selected, spanning a range of chronic atmospheric N inputs from 0.2 to 2.0 g m⁻² yr⁻¹. DIN as well as DON concentrations increased with N deposition, the latter increasing at a sharper incline. The increase in DIN concentrations was related to the reduced capacity of the moss layer to trap atmospheric N, which in turn was a result of N saturation of the moss layer. The enhanced DON concentrations appear to be a consequence of increased leaching of organic N compounds by *Sphagnum*. The importance of DON on N biogeochemistry in bogs opens new perspectives in relation to nutrient limitation and organic matter turnover.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1615 Global Change: Biogeochemical processes (4805); 1851 Hydrology: Plant ecology; 1890 Hydrology: Wetlands; **KEYWORDS:** bog, DIN, DON, eutrophication, global change, *Sphagnum*

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1. Introduction

[2] Industrial and agricultural activities have led to dramatic increases in the emissions of biologically active nitrogen (N) [Galloway *et al.*, 1995], often altering the composition and functioning of ecosystems. Some of the major environmental consequences are related to acidification and eutrophication of aquatic and terrestrial ecosystems [Vitousek *et al.*, 1997], as well as to the loss of biodiversity in many natural habitats [Jefferies and Maron, 1997; Stevens *et al.*, 2004]. Concerns related to altered atmospheric N supply become more important when anthropogenic N emissions do not decrease over time on a global scale [Stoddard *et al.*, 1999].

[3] Alteration of atmospheric precipitation chemistry can be assumed to play a paramount role in those ecosystems where nutrient and mineral supplies are totally dependent on atmospheric deposition, such as ombrotrophic peatlands or bogs. Bogs are typically wet, acidic ecosystems in which reduced decomposition favors peat accumulation. Few vascular plant species are found in bogs (mainly sedges, ericaceous and carnivorous plants), whereas the bulk of living and dead biomass is formed by *Sphagnum* mosses. In bogs, nitrification and nitrogen fixation take place at very low rates compared to other ecosystems because microbial

activity is hampered [Hemond, 1983; Bridgham *et al.*, 1998]. *Sphagnum* mosses thrive in bogs thanks to their ability to efficiently trap atmospheric deposition [Urban *et al.*, 1988], whereas vascular plants mainly rely on N released during decomposition processes [Aerts *et al.*, 1999]. Increasing levels of atmospheric N input are responsible for altering the nutrient limitation of *Sphagnum* mosses and causing a reduction in growth [e.g., Limpens and Berendse, 2003; Bragazza *et al.*, 2004]. Consequently, the ability of the *Sphagnum* layer to retain atmospheric N decreases, leading to higher concentrations of dissolved inorganic N concentration (DIN) in the bog water where it is available for vascular plants [Lamers *et al.*, 2000]. Enhanced N availability in the rhizosphere is expected to stimulate the expansion of vascular species and be detrimental to *Sphagnum* mosses [Heijmans *et al.*, 2002].

[4] Until now, research on bog water chemistry has mainly focused on the analysis of inorganic N, whereas data on organic N are generally lacking. This is remarkable, since many plants and mosses may also take up and assimilate organic N [Kielland, 1997; Lipson and Näsholm, 2001]. In addition, organic N has been shown to be an important component of the total dissolved N (TDN) in the organic horizon of forest ecosystems [e.g., Michalzik *et al.*, 2001; Perakis and Hedin, 2002].

[5] Here we assess the relationship between increasing levels of atmospheric N deposition and dissolved organic and inorganic N concentrations in European ombrotrophic

Table 1. List of Bogs Investigated With Geographical Position (Latitude and Longitude), Total Annual Precipitation, Nitrogen (N) Bulk Deposition (Including Bulk NO_3^- -N and NH_4^+ -N Deposition, Respectively), Mean (\pm s.d.) N Content in *Sphagnum* Capitula, and Mean (\pm s.d.) Relative Contribution of Dissolved Organic (DON) and Inorganic (DIN) Nitrogen to Total Dissolved N (TDN) Concentration in Bog Water^a

Bog and Country	Geographical Position	Annual Precipitation, mm	Total N Deposition (NO_3^- -N & NH_4^+ -N), $\text{g m}^{-2} \text{yr}^{-1}$	Mean N Content (\pm s.d.) in <i>Sphagnum</i> Capitula, %	Mean Relative (\pm s.d.) Contribution in Bog Waters	
					DON/TDN	DIN/TDN
Malmmyran - Norway	63°41'N 8°28'E	1200	0.2 (0.1 and 0.1)	0.61 (0.06)	82% (7%)	18%
Mrtvý luh - Czech Republic	48°52'N 13°53'E	700	0.5 (0.3 and 0.2)	0.97 (0.20)	61% (6%)	39%
Etang de la Gruere - Switzerland	47°14'N 7°03'E	1200	0.6 (0.3 and 0.3)	0.99 (0.15)	81% (2%)	19%
Wölfl Moor - Italy	46°26'N 11°24'E	808	0.8 (0.4 and 0.4)	0.90 (0.06)	73% (12%)	27%
Čihadla - Czech Republic	49°59'N 13°49'E	1470	1.9 (0.8 and 1.1)	1.34 (0.15)	66% (1%)	34%
Reigersplas - Netherlands	52°50'N 6°27'E	780	2.0 (0.6 and 1.4)	1.20 (0.12)	77% (6%)	23%

^aPrecipitation chemistry sources were: NILU-Norsk Institutt for Luftforskning; Český hydrometeorologický ústav; OFEFP/NABEL; *Tait and Thaler* [2000]; Rijksinstituut voor Volksgezondheid en milieu.

peatlands. In the present survey we decided to substitute space for time, i.e., to collect data under a natural gradient of atmospheric N deposition with the main advantage of detecting N concentration trends in bog water under relatively low, but chronic, additions of atmospheric N, thereby avoiding possible toxic effects of abrupt N inputs associated with short-term fertilization experiments.

2. Materials and Methods

2.1. Sampling Protocol

[6] Sampling was carried out at six European bogs during the period 2001–2003 mainly at the end of the growing season (Table 1). In order to limit the interbog variability related to (micro)-hydrological conditions, we collected all samples in plots characterized by similar moss composition, relying on the assumption that *Sphagnum* plants are good indicators of the mean water table position [i.e., *Clymo and Hayward*, 1982]. At each bog, three plots dominated by *Sphagnum fuscum* (Schimp.) Klinggr. and three plots dominated by *Sphagnum magellanicum* Brid. or *Sphagnum papillosum* Lindb. were selected in the central, ombrotrophic sector of the bog. The first species is characterized as a hummock species and indicative of drier micro sites, whereas the latter two species are lawn species and indicate wetter microhabitats. In each plot, all *Sphagnum* mosses were removed from a 100 cm² quadrat. Three water samples were collected close to the *Sphagnum* sampling area. Water was siphoned from free-standing water by means of a syringe and immediately filtered in the field through a 0.45- μm Whatman filter.

[7] Data on NO_3^- -N, NH_4^+ -N, and Cl^- precipitation chemistry were obtained from national organizations responsible for bulk deposition monitoring (Table 1). At each bog, mean bulk atmospheric N deposition was mostly calculated from data for the 3 years preceding the sampling year. The mean distance of monitoring stations from study bogs was about 37 km.

2.2. Chemical Analyses

[8] As the apical end (capitulum) is the most active growing part of *Sphagnum* mosses, capitula of all *Sphagnum* individuals were collected immediately after sampling. Before chemical analyses, capitula were ground

in a titanium mill through a 0.2-mm screen to ensure sample homogeneity. Subsamples were oven dried for 48 hours at 70°C to convert air dry-weight element concentrations to standard oven-dry conditions.

[9] Total N concentration in *Sphagnum* mosses was determined with an elemental analyzer (EA 1110, Carlo Erba). Standard reference material (NIST Citrus leaves 1572, National Bureau of Standards) was analyzed with the *Sphagnum* samples to ensure accuracy within 5% of known total N concentration.

[10] Water samples were analyzed colorimetrically using a continuous flow analyzer (FLOWSYS, Systeaa, Italy) for Cl^- , NO_3^- -N, and NH_4^+ -N. Total dissolved N (TDN) was determined as NO_3^- -N after persulphate-UV digestion and N reduction by copperized cadmium. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and dissolved inorganic (NO_3^- -N plus NH_4^+ -N) nitrogen (DIN). Instrumental detection limit for NO_3^- -N was 0.5 ppb, and the average relative percentage difference in the concentrations of known N-standards in replicate analyses was 5.5% (range 2–11%).

[11] To permit the use of the water chemistry data of samples collected in different years in different bogs situated in different climate zones, the concentrations of DIN and DON were corrected for the effect of evaporation by dividing the N concentration with the quotient $\text{Cl}_{\text{pore water}}^- / \text{Cl}_{\text{rain}}^-$, based on the conservative behavior of chlorine in bog water [Appelo and Postma, 1994].

3. Results

[12] N concentrations in *Sphagnum* capitula increased linearly with atmospheric N deposition ($R^2 = 0.78$, $p = 0.02$), ranging from about 0.6% at low deposition sites in Norway, to about 1.3% at high deposition sites in the Netherlands and the Czech Republic (Table 1). The contribution of organic N forms to TDN in bog waters ranged between 60% and 80%, whereas the contribution of inorganic N forms ranged between 20% and 40% (Table 1). The ratio between DIN and DON was not significantly affected by N deposition (Pearson's correlation coefficient = -0.27 , $p = 0.28$, $n = 18$).

[13] Both DIN and DON concentrations increased linearly with N deposition, with the DON concentration typically

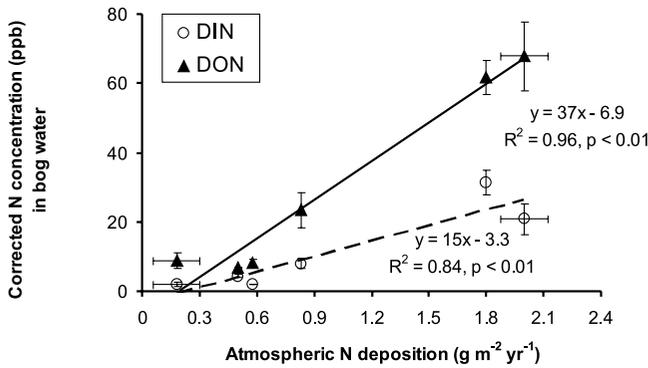


Figure 1. Relationships between mean (\pm s.d.) dissolved organic (DON) and inorganic (DIN) nitrogen concentration with atmospheric N deposition at six European bogs. Standard deviations of atmospheric N deposition are reported only for the lowest and the highest values, to avoid cluttering the figure. Concentrations of dissolved N are based on three replicates at each bog and have been corrected taking into account the effect of evapotranspiration (see text for details).

remaining up to 3 times higher than DIN concentration (Figure 1). Additionally, the DIN and DON concentrations were positively related to the N concentration in the *Sphagnum* capitula, with the latter increasing at a steeper rate (Figure 2).

4. Discussion

[14] Our results show that DON concentrations exceed those of DIN in bogs and that the difference between DON and DIN concentrations increased with increasing inputs of atmospheric N. The observed relationship between TDN and atmospheric N deposition supports early work by *Yesmin et al.* [1995] and *Williams et al.* [1999], who showed an increase of DON concentrations under artificial addition of inorganic N in bogs, and work by *Lamers et al.* [2000], *Bragazza et al.* [2003], and *Limpens et al.* [2003], who showed a relationship between DIN in bogs and atmospheric N input.

[15] There is evidence that atmospherically deposited inorganic N does not contribute directly to the increase of DON concentration in bogs, as the amount of inorganic nitrogen that is incorporated into DON has been demonstrated to be negligible [*Williams et al.*, 1999]. In addition, direct effects of atmospherically supplied organic N on the DON concentrations of bog waters can likely be excluded. Indeed, although atmospheric organic N deposition can contribute up to 23% of total N dissolved in European precipitation [*Cornell et al.*, 2003], on a global scale, there are no indications that the amount of organic N deposited by rain increases with N deposition [*Neff et al.*, 2002]. In addition, the rainwater concentrations of DON for continental areas showed mean values lower than DON concentration reported for bog waters [*Yesmin et al.*, 1995; *Adamson et al.*, 1998; *Cornell et al.*, 2003].

[16] The microbial community does not seem to be a source of the increased DON concentrations either, as suggested by *Kalbitz and Geyer* [2002], who found low microbial modification of DON after nitrogen isotopic analyses of peat. The above is further supported by fertilization experiments conducted by *Williams and Silcock* [2000]. They found that the addition of inorganic N to bogs does not affect microbial production, but rather increases the stability of microbial community, dampening the seasonal fluctuations of microbial biomass. On account of the above, it seems reasonable to assume that atmospheric N deposition affects the DON concentration via its effect on the plant community; in the case of bogs, we suggest a prominent role of *Sphagnum* plant metabolism.

[17] The positive relationship between DIN concentration in bog water and N concentration in *Sphagnum* mosses reflects the preceding N saturation of the *Sphagnum* layer and the associated decrease in the capacity of the moss layer to retain the deposited N. Indeed, in pristine conditions, *Sphagnum* mosses are typically N-limited, relying on an efficient trapping of the small quantity of N supplied by wet and dry deposition [*Li and Vitt*, 1997]. Under increasing inorganic N input, *Sphagnum* mosses actively absorb the excess exogenous N until a saturation state is reached where N is no longer growth limiting [*Bragazza et al.*, 2004]. In such a situation the moss layer fails to effectively absorb atmospherically supplied inorganic N, which can freely pass through the surface moss layer to reach the water table [*Limpens et al.*, 2003].

[18] The significant relationship between the N tissue concentration in *Sphagnum* mosses and DON concentration in bog water suggests that living *Sphagnum* affect the DON concentration, presumably by leaching organic N compounds. As very little or no N deposited over a bog is

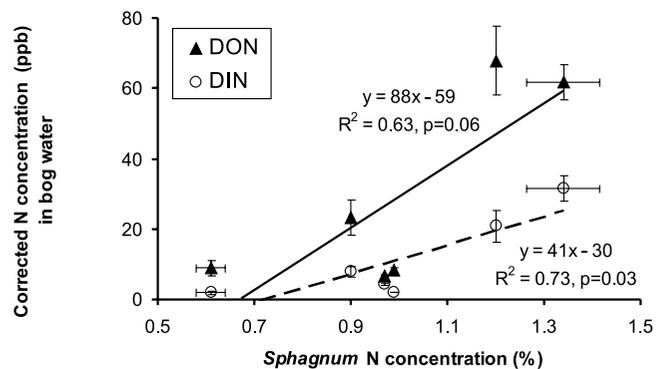


Figure 2. Relationships between mean (\pm s.d.) DON and DIN concentration with mean nitrogen (N) concentration in *Sphagnum* capitula measured in six European bogs. Data are six replicates (*Sphagnum* samples) and three replicates (water samples) at each bog. Standard deviations of *Sphagnum* N concentration are reported only for the lowest and the highest values to avoid cluttering the figure (for all s.d. values, see Table 1). Concentrations of dissolved N have been corrected taking into account the effect of evapotranspiration (see text for details).

directly incorporated into DON, DIN, or the microbial N pool [Williams *et al.*, 1999], the primary source of organic N compounds appears to be organic compounds from the *Sphagnum* mosses themselves [McKnight *et al.*, 1985; Williams and Silcock, 2000]. This hypothesis is consistent with the enhanced production of amino acids by *Sphagnum* mosses under increasing levels of atmospheric N deposition, a metabolic mechanism adopted to avoid toxic effects of increased N absorption [Baxter *et al.*, 1992; Nordin and Gunnarsson, 2000]. Results from Adamson *et al.* [1998] further support the role of living *Sphagnum* mosses as a source of DON. Indeed, the authors measured DON concentrations at different depths along the peat profile, and found the highest concentrations of DON in the surface water, where *Sphagnum* is metabolically active [McKnight *et al.*, 1985].

[19] The role of plant exudates in affecting bog biogeochemistry has also been recently claimed by Freeman *et al.* [2004] to explain the rising exports of dissolved organic carbon (DOC) from bogs under elevated CO₂ levels. The authors suggest that when nutrient availability increases, net primary production of bog plants is stimulated and becomes more sensitive to increased CO₂ levels, resulting in an enhanced leaching of carbon into the soil [see also Fenner *et al.*, 2004]. Our data on dissolved N seem to support the above, suggesting that under increasing levels of both atmospheric N deposition and CO₂, bog plants benefit from a sort of double fertilization, which enhances the release of C and N through plant exudates.

[20] In conclusion, our findings have for the first time demonstrated that in European ombrotrophic peatlands, organic N is the major component of TDN forms, even under chronic, increasing rates of atmospheric N input. Since DON concentrations increase more strongly than DIN concentrations under increasing atmospheric N inputs, it is important to take into account the organic component of dissolved N in peat-producing ecosystems when studying the impact of N pollution on the competitive balance between plant species, as well as the export of N from N saturated ecosystems.

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