Regional variability in the atmospheric nitrogen deposition signal and its transfer to the sediment record in Greenland lakes


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Abstract

Disruption of the nitrogen cycle is a major component of global environmental change. δ¹⁵N in lake sediments is increasingly used as a measure of reactive nitrogen input but problematically, the characteristic depleted δ¹⁵N signal is not recorded at all sites. We used a regionally replicated sampling strategy along a precipitation and N-deposition gradient in SW Greenland to assess the factors determining the strength of δ¹⁵N signal in lake sediment cores. Analyses of snowpack N and δ¹⁵N-NO₃ and water chemistry were coupled with bulk sediment δ¹⁵N. Study sites cover a gradient of snowpack δ¹⁵N (ice sheet: ~26%; coast: ~10%), atmospheric N deposition (ice sheet margin: ~0.2 kg ha⁻¹ yr⁻¹; coast: ~0.4 kg ha⁻¹ yr⁻¹) and limnology. Three ²¹⁰Pb-dated sediment cores from coastal lakes showed a decline in δ¹⁵N of ca. ~1‰ from ~1860, reflecting the strongly depleted δ¹⁵N of snowpack N, lower in-lake total N (TN) concentration (~300 µg N L⁻¹) and a higher TN-load. Coastal lakes have 3.7–7.1× more snowpack input of nitrate than inland sites, while for total deposition the values are 1.7–3.6× greater for lake and whole catchment deposition. At inland sites and lakes close to the ice-sheet margin, a lower atmospheric N deposition rate and larger in-lake TN pool resulted in greater reliance on N-fixation and recycling (mean sediment δ¹⁵N is 0.5–2.5‰ in most inland lakes; n = 6). The primary control of the transfer of the atmospheric δ¹⁵N deposition signal to lake sediments is the magnitude of external N inputs relative to the in-lake N-pool.

The disruption of the nitrogen cycle is now a major component of global environmental change and is an unambiguous indication of anthropogenic impact during the last 150–200 yr (i.e., the Anthropocene) (Wolfe et al. 2013; Waters et al. 2016). Industrial fixation of reactive nitrogen (Nr) plus that resulting from fossil fuel burning is now more than that fixed naturally and continues to increase rapidly (Galloway et al. 2008). The impacts of Nr on ecosystem structure and productivity are well known, largely through studies on low-land, agriculturally dominated landscapes (Smith et al. 2006). However, arctic and alpine ecosystems are nutrient poor, highly sensitive to disturbance and adapted to low N availability (Dormann and Woodin 2002). Although far removed from the main Nr sources with correspondingly low N-deposition rates (generally ~0.5–1 kg ha⁻¹ yr⁻¹; Burkhart et al. 2004; AMAP 2006), the susceptibility of these remote high latitude ecosystems to chronic long-term N-additions is not well constrained (Street et al. 2015).

Although nonvascular cryptogam species (including mosses and lichens), which are an important component of terrestrial ecosystems at high latitudes have been shown to be highly efficient at utilizing available N (Curtis et al. 2006), the occurrences of these species may be restricted by chronic N-deficiency.
2005), it is still not fully understood how biological N retention and physiological function is affected by low and sustained N enrichment over decades. Many experiments use N additions that represent greater inputs than local atmospheric Nr deposition rates and are typically short-term (<5 yr). Tye et al. (2005) found that up to 60% of N added experimentally (as N-NO$_3^-$) to snowpack on Svalbard was immobilized (mainly as organic N). However, with up to 40% of the added N “lost” to the system, there was a high possibility of N-transfer to aquatic systems. This is especially likely at high altitudes where reduced vegetation cover (e.g., fell-field) limits the ability of the terrestrial system to retain or process excess Nr. Although N deposition rates across the Arctic are low (Burkhart et al. 2004; AMAP 2006), they are sustained over decades and the sensitivity of these ecosystems to additional inputs of N above natural background rates suggests that critical loads at which ecosystem change occurs will also be low (Pardo et al. 2011; Saros et al. 2011).

The timescale of anthropogenic disruption of the N-cycle is broadly known (Galloway et al. 2004) and is confirmed by modeling exercises and ice core records (Posch et al. 2012; Wolff 2013). Records of N concentration in large ice sheets represent temporally accurate records of atmospheric N deposition at the hemispheric scale (i.e., the Greenland record) (Mayewski et al. 1986) while ice caps are more spatially variable and perhaps reflect regional variability in emissions and deposition (Goto-Azuma and Koerner 2001). At a small spatial scale (e.g., local, 1–10 km$^2$), it is more problematic to determine atmospheric N-loads delivered to lakes and their catchments from ice core records because of the inherent variability of retention, processing, and transfer by soils and vegetation, as well as the vagaries of hydrology, topography/morphometry, and precipitation (Seastedt et al. 2004; Catalan et al. 2009). While it is clear that sensitive arctic and alpine lakes have been affected by increased N deposition from anthropogenic sources (Wolfe et al. 2013), the exact mechanisms that give rise to observed changes in N biogeochemistry of remote lakes throughout the northern hemisphere remain undetermined and requires further work to elucidate the processes involved. The stable isotope composition of lake sediment (δ$^{15}$N organic matter) has been used as an indicator of N deposition loads in Arctic lakes (Hobbs et al. 2011) but a central problem remains why do some remote lakes record a 20$^{th}$ Century δ$^{15}$N depletion signal while others (often neighboring sites) do not? This is an important issue as δ$^{15}$N in lake sediments offers one of the few means of identifying a N-effect on remote lakes over historic timescales and is central to the climate-nutrient debate (Wolfe et al. 2013). Lake sediment records indicate that there is substantial community change over the last 100–150 yr in arctic lakes but the main driver is unclear: is it regional warming or long-range atmospheric deposition of nutrients (Catalan et al. 2009)?

Because of the impact of industrial N-fixation on the N-cycle, volatile N produced by industrial activity is isotopically depleted (Heaton 1986; Hastings et al. 2009); it is widely assumed that this depleted δ$^{15}$N-Nr signal will be transferred to and recorded in lake sediments. However, lake δ$^{15}$N is a function of both atmospheric inputs, catchment, and in-lake processing (Talbot 2001). Sediment records reflect these more local/regional signals of changing N inputs to aquatic ecosystems but can also be problematic to interpret due to the dynamic nature of N following incorporation in sediments (Kendall et al. 2007). Change in sediment δ$^{15}$N from remote lake paleo-records is now considered to be a faithful indicator of increased Nr input to lakes over the last 150 yr, although this relationship has not been demonstrated unequivocally (Holtgrieve et al. 2011). At many sites, the timing of change in the δ$^{15}$N record in lake sediments agrees with variation in biological indicators of ecological change (e.g., diatom community turnover, algal pigment concentration) and is broadly interpreted as evidence of increasing aquatic production. However, there are a similar number of sites where the δ$^{15}$N sediment record is ambiguous (Curtis and Simpson 2011; Hobbs et al. 2016) and does not correlate with historical patterns of atmospheric Nr deposition and/or ecological change. Although it has been suggested that this variability reflects interactions between Nr deposition and climate variability (Hobbs et al. 2016), in-lake processing (i.e., anoxic hypolimnion, denitrification, and trophic interactions) and/or post-depositional diageneis, these processes are not well understood and are variable among individual sites. For example, lakes in similar geographic regions can show variable trends in the sediment δ$^{15}$N record (Curtis and Simpson 2011). At remote, high latitude sites, where long term Nr deposition records do not exist, there are few, if any, studies, that have attempted to match contemporary δ$^{15}$N signals in precipitation and trace it through into the lake sediment record (Hobbs et al. 2016). The divergent lake δ$^{15}$N records within a region has been taken by some as an indication of a lack of an atmospheric N pollution signal at high latitudes and has therefore stymied the discussion about what is driving the ecological change (Catalan et al. 2013).

Given the problem of complex ecological responses to multiple anthropogenic stressors/drivers which operate over the same temporal scale (e.g., warming, greening, atmospheric pollution), across the Arctic, it is important to have an independent measure of changing N inputs at remote sites to allow for a nuanced assessment of what is driving ecological change. The natural environmental experimental framework provided by SW Greenland (no mid-late-20$^{th}$ century warming) (Mermild et al. 2014) allows some of these possible drivers to be assessed in a controlled, systematic manner. In an attempt to resolve the issue of the impact of change in Nr deposition load on remote lakes and the transfer of the depleted δ$^{15}$N signal from precipitation to lake sediments, we studied lakes in three groups located across a precipitation (climate) and N deposition gradient in SW Greenland. We used an integrated, regionally replicated sampling strategy across gradients of precipitation, vegetation
and limnology and incorporate snow-pack chemistry, in-lake N concentration and stable isotope analyses of 210Pb-dated lake sediments. Through the analysis of 12 lake-catchments located across the Kangerlussuaq region that cover differences in nitrogen isotopic composition of precipitation and N flux (Curtis et al. 2018), we tested three hypotheses: first that the $\delta^{15}N$ record of organic matter in sediment cores is a direct reflection of the input $\delta^{15}N$ signature; second, that the regional variation in bulk $\delta^{15}N$ in sediment cores and their change over time reflects differences in limnology rather than N input fluxes and third, that hydrological connectivity between lakes and their catchment is of limited relevance.

Methods

Study area

The Kangerlussuaq region between 66.5–67.2°N and 50–53.5°W forms part of the widest ice free margin in SW Greenland (Fig. 1). There is a natural climate gradient: mean annual precipitation increases from < 250 mm yr$^{-1}$ close to the ice sheet margin to > 600 mm yr$^{-1}$ at the coast (Mernild et al. 2015). Across the region, terrestrial vegetation is classified as dwarf shrub tundra, dominated by Betula nana, Salix glauca, Empetrum spp., and Vaccinium spp. with grasses and cryptogams also common. Close to the ice sheet margin, Ledum palustre heath, S. glauca heath, and Carex stupina steppe are, however, more abundant, while toward the coast, Empetrum spp., bryophytes, and lichens are increasingly common. The geology is relatively uniform, principally composed of granodioritic gneisses and the region is at the southernmost zone of continuous permafrost in Greenland (Nielsen 2010).

The study was based on three discrete clusters of lake catchments along a precipitation and N deposition gradient from the ice sheet margin to the coast, hereafter referred to as ice sheet, inland, and coastal sites (Fig. 1). The distances between study locations are an order of magnitude greater than the distance between lake-catchments within each location; the inland sites are ~ 60 km from the closest coastal site and 34 km from the closest ice sheet site (Fig. 1).

Study lakes and limnology

The region is a major lake district containing > 20,000 lakes. The study lakes are all small (< 40 ha), glacially scoured basins which are oligotrophic (0.45 ± 0.07 µg Chl a L$^{-1}$) and chemically dilute (< 600 µS cm$^{-1}$; c. 35–2000 µg TN L$^{-1}$; 3–30 µg total phosphorus (TP) L$^{-1}$; Whiteford et al. 2016) (Table 1). Reference is also made to four previously
Table 1. Annual nitrate deposition as a percentage of lake TN pool calculated using four methods with varying assumptions as outlined below. See also main text. Cmt, catchment.

<table>
<thead>
<tr>
<th>Region</th>
<th>Lake</th>
<th>$\delta^{15}N$ lake snow</th>
<th>$\delta^{15}N$ cmt</th>
<th>N pools and inputs (kg)</th>
<th>Inputs as % of lake TN pool</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lake snow</td>
<td>Lake TN</td>
<td>Lake deposition</td>
</tr>
<tr>
<td>Ice sheet</td>
<td>SS901*</td>
<td>−7.7</td>
<td>−7.5</td>
<td>490</td>
<td>0.11</td>
<td>2.33</td>
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<tr>
<td>Ice sheet</td>
<td>SS903</td>
<td>−6.4</td>
<td>−6.7</td>
<td>3095</td>
<td>0.40</td>
<td>1.89</td>
</tr>
<tr>
<td>Ice sheet</td>
<td>SS904</td>
<td>−9.1</td>
<td>−8</td>
<td>316</td>
<td>0.04</td>
<td>0.71</td>
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<td>Inland</td>
<td>SS2</td>
<td>−3.6</td>
<td>−3.5</td>
<td>1587</td>
<td>0.56</td>
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<td>Inland</td>
<td>SS8</td>
<td>−7.2</td>
<td>−5.6</td>
<td>765</td>
<td>0.18</td>
<td>3.92</td>
</tr>
<tr>
<td>Inland</td>
<td>SS1341*</td>
<td>−6.2</td>
<td>−5.6</td>
<td>364</td>
<td>0.10</td>
<td>0.56</td>
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<td>Coast</td>
<td>AT7</td>
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<td>−11.8</td>
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<td>0.13</td>
<td>6.55</td>
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<tr>
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<td>AT1</td>
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<td>−11.6</td>
<td>51</td>
<td>0.17</td>
<td>1.86</td>
</tr>
<tr>
<td>Coast</td>
<td>AT6*</td>
<td>−12.1</td>
<td>−11.1</td>
<td>198</td>
<td>0.26</td>
<td>15.37</td>
</tr>
<tr>
<td>Coast</td>
<td>SS49*</td>
<td>−12.1</td>
<td>−11.3</td>
<td>196</td>
<td>0.49</td>
<td>7.98</td>
</tr>
</tbody>
</table>

* No site specific snowpack data, regional means used.

SNOWPACK ESTIMATES

Lake snow: nitrate pool in lake ice snowpack as % of lake TN pool.

Catchment snow: nitrate pool in catchment snowpack as % of lake TN pool.

Direct deposition: estimated annual nitrate deposition to lake surface as % of lake TN pool.

Deposition vs. lake chemistry comparisons

Without detailed catchment hydrology and chemical data, it is not possible to accurately determine the deposition input fluxes to the study lakes. At the catchment scale, there are likely to be major differences in the proportion of deposition reaching lakes through surface runoff, which is negligible in the inland lakes but could be much more important at the coast. Here, we estimate the range of possible NO$_3^-$ and NH$_4^+$ deposition inputs to lakes relative to total N (TN) pools in the lakes using four methods with two contrasting assumptions. Under the first scenario, we assume that a pulsed input of snowmelt represents the key input of atmospheric NO$_3^-$ into the system, as nitrate accumulated over the winter period is delivered in a relatively short period of intense biological activity. Although the proportion of accumulated catchment snowpack which enters the lake as...
meltwater is not known, we can estimate the minimum and maximum bounding values as follows: first, the minimum snowpack estimate assumes that all snowpack NO\textsubscript{3}\textsuperscript{-} inputs to the lake would occur if the soil is frozen and biological activity is minimal, so that all snowmelt could drain into the lake basin and for closed basins, would then be delivered as the lake ice melts. In reality, losses through surface flow out of the catchment may occur, but our estimate provides the theoretical maximum input from snowpack.

Alternatively, if it is assumed that the key determinant of atmospheric NO\textsubscript{3}\textsuperscript{-} inputs is the annual deposition flux, then we can estimate the minimum and maximum bounding fluxes in a similar way, based on direct deposition to the lake surface and deposition to the entire catchment. In this third approach, NO\textsubscript{3}\textsuperscript{-} deposited directly to the lake surface through the whole year (rainfall and snowpack) is estimated using lake area and regional deposition flux from Curtis et al. (2018) (but ignoring the meltwater routing issue raised above). Finally and fourth, annual nitrate deposition onto the whole lake catchment provides the maximum bounding flux for atmospheric NO\textsubscript{3}\textsuperscript{-} entering lake systems, while recognizing that a large proportion will in reality be taken up and/or immobilized in catchment soils and vegetation before reaching the lake during the summer when soils are not frozen.

Using these four estimates of inputs, the ratio of annual inputs to the lake TN pool may be expressed as a percentage to provide an index of the strength of the input signal. Lake TN pools are estimated using mean lake water TN concentration, lake surface area, and mean depth estimated as 0.5× maximum depth. Catchment and lake areas were obtained from manually digitized boundaries on topographic maps.

**Sediment cores**

Sediment profiles were taken in 2010 and 2011 from the deepest part of each lake using a HON-Kajak gravity corer (Renberg 1991). Intact sequences from the sediment-water interface to a depth of ~30 cm were recovered and were extruded on site at a resolution of 0.25 cm or 0.5 cm intervals. All samples were stored frozen until further analysis. Following standard analyses for percent dry weight and organic content (loss-on-ignition at 550\degree C), samples were freeze dried. Each profile was analyzed for \textsuperscript{210}Pb, \textsuperscript{226}Ra, \textsuperscript{137}Cs, and \textsuperscript{241}Am by direct gamma assay and chronologies derived using the CRS model (Appleby 2001). Details of the \textsuperscript{210}Pb chronologies are provided in the Supporting Information Figs. S1–S12. Chronologies for cores from lakes SS2 and SS903 are taken from Sobek et al. (2014) while those for the four lakes which were previously analyzed for \delta\textsuperscript{15}N, the \textsuperscript{210}Pb results can be found elsewhere (Bindler et al. 2001a,b; Perren et al. 2009; Reuss et al. 2013).

**Sediment stable isotope analyses**

Subsamples of sediment were milled to a fine powder using a Retsch mixer mill. Approximately 1 mg of milled sediment was transferred to pre-weighed tin capsules, which were then sealed. The amount of dried sediment in each capsule was recorded. The samples were analyzed for TN, and \textsuperscript{15}N/\textsuperscript{14}N on a Flash EA 1112 connected to a Thermo Finnigan Delta V isotope ratio mass spectrometer via a CONFLO IV at the Bloomsbury Isotope Facility (University College London). The isotopic ratio of \textsuperscript{15}N/\textsuperscript{14}N is expressed using the delta (\delta) notation in parts per thousand (or per mille, \%\textsubscript{oo}), where \delta\textsuperscript{15}N\textsubscript{oo} = [(R\textsubscript{sample}/R\textsubscript{standard} – 1) × 1000, where \textit{R} is the \textsuperscript{15}N/\textsuperscript{14}N ratio in the measured sample or the appropriate standard. The standard for nitrogen is the \delta\textsuperscript{15}N of atmospheric nitrogen (commonly referred to as Air).

**Results**

**Snowpack and deposition**

Snowpack nitrate concentration varies regionally; from 1.5 \mu eq L\textsuperscript{-1} at the coast to 2.4 \mu eq L\textsuperscript{-1} at the ice margin. Snowpack depth is greatest at the coast (>180 mm snow water equivalent [SWE]) compared to inland (<44 mm SWE) and the ice sheet margin (36 mm SWE) (Curtis et al. 2018). This leads to inverse fluxes along the regional transect: 0.13 kg NO\textsubscript{3}\textsuperscript{-}N ha\textsuperscript{-1} yr\textsuperscript{-1} at the coast, compared to 0.08 kg NO\textsubscript{3}\textsuperscript{-}N ha\textsuperscript{-1} yr\textsuperscript{-1} inland and 0.11 kg NO\textsubscript{3}\textsuperscript{-}N ha\textsuperscript{-1} yr\textsuperscript{-1} at the ice sheet margin (Fig. 2). There are statistically significant regional differences in wet NH\textsubscript{3} deposition, ~0.24 kg N ha\textsuperscript{-1} yr\textsuperscript{-1} at the coast and 0.05 kg ha\textsuperscript{-1} yr\textsuperscript{-1} and 0.09 kg ha\textsuperscript{-1} yr\textsuperscript{-1} at the inland and ice margin lakes, respectively. As a result, the total dissolved inorganic nitrogen (DIN) flux is twofold greater at the coast compared to the ice margin (0.37 kg ha\textsuperscript{-1} yr\textsuperscript{-1} vs. 0.19 kg ha\textsuperscript{-1} yr\textsuperscript{-1}). The \delta\textsuperscript{15}N in snowpack ranged between −7.5\%\textsubscript{oo} and −5.7\%\textsubscript{oo} at the inland and ice margin sites, and −11.3\%\textsubscript{oo} at the coast. There are clear regional differences in the relative magnitude of snowmelt inputs and deposition fluxes compared to lake TN pools (Table 1). If the complexities of snowmelt pathways are ignored, snowpack fluxes of NO\textsubscript{3}\textsuperscript{-} to lake surfaces at the coast are at least 3.7× greater as a proportion of lake TN than at the inland sites while the NO\textsubscript{3}\textsuperscript{-} pool in the entire catchment snowpack relative to lake TN pools is at least 7.1× greater for coastal lakes (Table 1). For annual deposition fluxes, direct deposition to the lake surface as a proportion of lake TN pool is at least 1.7× greater at the coast, while using total deposition to the entire catchment gives ratios at least 3.6× larger for coastal lakes.
Limnology

There are strong regional differences in the water chemistry and physical limnology along the ice margin-coast transect, most notably the higher conductivity and dissolved organic carbon (DOC) concentrations observed in the inland lakes at the head of the fjord (close to Kangerlussuaq) (Table 2) (see also Anderson et al. 2001; Whiteford et al. 2016). These lakes also have the highest TN concentration, strong stratification, and hypolimnetic anoxia with increased NH$_4^+$ at depth. Both the coastal and ice margin lakes are oligotrophic and dilute with oxic hypolimnia, but there are statistically significant differences between these lake groups lakes in terms of pH (coastal lakes are slightly acidic), DOC and TN, which are higher inland (Table 2). While mean lake NO$_3^-$ concentration is higher at the coast, there is a distinct seasonal pattern in DIN availability in all three lake clusters: the concentration of NO$_3^-$ and NH$_4^+$ is highest under-ice and both ions are rapidly depleted with the onset of increased biological production.

Sediment dating and $\delta^{15}N$

Sediment accumulation rates are low at all sites (generally around 0.05 cm yr$^{-1}$ or less) (Supporting Information Table 1) but are particularly low in the coastal and ice margin lakes. The ice margin lakes all have positive $\delta^{15}N$ sediment values (1.2–1.9‰) and there are few systematic temporal trends although at SS903, $\delta^{15}N$ sediment decreased slightly from 2.3‰ to 1.9‰ (Fig. 3). Two of the three inland lakes (SS8 and SS1341) exhibit little trend in $\delta^{15}N$ over the past ~ 100 yr, varying between 0.46‰ and 1.3‰ while at SS2, $\delta^{15}N$ increased in the sediment record from 1.8‰ ~ 1800AD to 2.7‰ at the surface (2010 AD) (Fig. 3). Three of the coastal lakes show systematic decreases of ~ 1‰ $\delta^{15}N$ from 1880–1900 AD to present, although the background values vary: AT6 decreases from 3.5‰ to 2.5‰, AT1 from 2.5‰ to 1.5‰ and SS49 from 1.4‰ to 0.5‰. There is no trend at AT7 apart from a positive increase of 0.6‰ from ~ 1994 AD onward, a pattern which is also observed at AT6 (Fig. 3). The C% and $\delta^{13}C$ profiles from the cores are shown in Supporting Information Fig. S13.

Discussion

The NO$_3^-$ concentration and $\delta^{15}N$-NO$_3^-$ record from the Greenland Summit ice core (Hastings et al. 2009) shows a significant increase in nitrate concentration beginning in the late 1800s and early 1900s and a substantial depletion in $\delta^{15}N$ of NO$_3^-$, falling from a pre-industrial average of ~ 11‰ to around 0‰ by the 1970s and has remained at this low level since (Fig. 4). However, of the 16 lakes that have been
Table 2. Chemical properties of study lakes. Values provided represent site-averages (± standard deviation) of three measurements taken at a depth of 0.1 m in all lakes available for all sampling occasions (n = 5–12).

<table>
<thead>
<tr>
<th>Location</th>
<th>Lake</th>
<th>Alkalinity (equiv L⁻¹)</th>
<th>Conductivity (μS cm⁻¹)</th>
<th>pH</th>
<th>DOC</th>
<th>TN</th>
<th>TP</th>
<th>DIN: SGP</th>
<th>NH₄⁺</th>
<th>NO₂⁻</th>
<th>NO₃⁻</th>
<th>SRP, soluble reactive phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice sheet</td>
<td>SS91</td>
<td>7.6 ± 0.7</td>
<td>1466 ± 2</td>
<td>7.9 ± 0.7</td>
<td>128 ± 2</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>7.3 ± 0.1</td>
<td>2190 ± 1</td>
<td>7.8 ± 0.9</td>
<td>367 ± 5</td>
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<td>1660 ± 6</td>
<td>8.0 ± 0.7</td>
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<td>1660 ± 6</td>
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Snow pack chemistry and regional N-deposition rates

There are few data on N deposition rates in the Arctic (AMAP 2006) and what are available are mainly derived from deposition models (Posch et al. 2012). Also, rates are generally assumed to be low and inconsequential for ecosystem functioning. There is, however, a paucity of data for recent atmospheric N-deposition rates across Greenland, although there have been studies of snowpack and ice core records of pollutants on the Greenland ice sheet (e.g., Dye3, 400 km distant from the present study site; Dye2, 550 km; Summit, 800 km distant) (Burkhart et al. 2006). The N deposition flux rates estimated for the Kangerlussuaq area of SW Greenland are low (< 1 kg ha⁻¹ yr⁻¹) (Curtis et al. 2018) and compare with a mean derived from snow pits at Summit of 0.5 kg NO₃⁻ ha⁻¹ yr⁻¹ (0.11 kg N-NO₃⁻ ha⁻¹ yr⁻¹; Burkhart et al., 2004); the latter are double the pre-industrial values for both wet and dry NO₃⁻ deposition (Fischer et al. 1998).

While the inorganic N deposition rates in this study are low, they exhibit a distinct regional pattern, reflecting broad precipitation patterns (Mernild et al. 2015) with a depleted δ¹⁵N signal at the coast (Fig. 2). Higher deposition of N at the coastal sites, despite lower snowpack concentrations of NO₃⁻, is due to greater precipitation at the coast, which not only increases rates of pollutant scavenging by wet deposition (Bindler et al. 2001b). Moreover, the high snowpack accumulation also reduces re-emission of NO₃⁻ to the atmosphere and minimizes the post-depositional process which would otherwise tend to enrich the snowpack δ¹⁵N signal (Curtis et al. 2018). The high concentration of ammonium in coastal snowpack is most likely to be due to marine emissions and aerosol deposition onto the snowpack, which the sea salt data show to be a critical process (Jones 1999; Pomeroy et al. 1999). While this makes a major contribution to lake total inorganic N inputs, there is no evidence from ice core records of increasing NH₄⁺ deposition over the past ~ 200 yr (Savarinio and Legrand 1998), hence we focus here on NO₃⁻ inputs and assume there has been no temporal trend in NH₄⁺ deposition.

The regional gradient in snowpack δ¹⁵N (Fig. 2) suggests strong fractionating processes between the coastal and inland/ice sheet margin sites. Higher levels of volatilization...
of NO$_3$ at the two inland locations with greater snow sublimation and lower precipitation may lead to enrichment of snowpack $^{15}$N compared with the coastal sites. Heaton et al. (2004) and Morin et al. (2008) suggested that post-deposition processing of snowpack nitrate would lead to isotopic enrichment, so while these processes cannot account for the low coastal values, they could account for the higher inland values if it is assumed that fresh snow in all locations was deposited with a similar $^{15}$N value of c. $-11\%_o$. Since snow photochemistry is a major driver of NO$_3$ re-emissions, the effects of post-depositional processing should be maximal in spring when UV exposure is highest and there is still snowpack present (Morin et al. 2008). The greater snowfall at the coast increases the burial rate of NO$_3$ in the snowpack and hence reduces re-emission rates and photolysis. Importantly, this more depleted $^{15}$N in the snow remaining on the lake ice at the coast is more effectively transferred to the lake water as snow melts in a relatively unaltered state due to the reduced fractionation.

**Sediment $^{15}$N in lakes**

Nitrogen cycling in lakes is complex. The $^{15}$N isotope signal of bulk sediment is influenced by the primary source of organic matter, fractionation during ammonia and nitrate assimilation from DIN, N fixation (direct assimilation of atmospheric nitrogen) as well as internal recycling of the organic nitrogen-DIN pool, in particular the processes of ammonification, nitrification, and denitrification (Teranes and Bernasconi 2000; Talbot 2001).

There are two main mechanisms proposed that could cause the observed depletion in $^{15}$N in sediment cores from remote, arctic lakes; (1) increased biological utilization of DIN and (2) increased deposition of isotopically light N from emission sources of fossil fuel combustion. The first mechanism is likely to result from an increased availability of N to lake biota until P becomes limiting, at which point, discrimination between the heavy and light isotopes would begin with incomplete usage of the DIN pool and the Rayleigh distillation effect can act to increase discrimination between reactant and product (Kendall et al. 2007). This process is unlikely to be relevant in SW Greenland lakes because of their oligotrophic nature. There is a clear N : P gradient, increasing from the ice margin to the coast (Table 2), which reflects the greater P load (form dust) close to the ice sheet (Hawkins et al. 2016) and increased N-load at the coast. Despite this increased N-load (Curtis et al. 2018) which has likely alleviated nutrient stress of primary producers to some extent, the coastal lakes remain nutrient poor (see next section). Regionally, all lakes are very nutrient poor and are N + P co-limited with all available DIN utilized very quickly by in-lake biological processes. Phytoplankton growth yield is greater with addition of both N and P (Whiteford unpubl.), supporting the assumption that algal discrimination of N is not a dominant process.

The second mechanism is one of isotope mixing, with an increased amount of "light" $^{14}$N acting to reduce the overall isotopic values of the DIN pool in lakes. Holtgrieve et al. (2011) hypothesized that the switch to isotopically lighter
organic matter in lake sediments is due directly to the large depletion in atmospheric NO$_3^-$ (as recorded in the Summit ice core). This process results in the incorporation of an isotopically light source of NO$_3^-$ by organisms, thereby causing the isotopic signature of the organic matter becoming progressively lighter ($\delta^{15}N$ depleted) over time and subsequently stored in the sediment records. This hypothesis gives little consideration to the role of transformations of deposited N in both lakes and catchment vegetation and soils and to the stimulation of aquatic and terrestrial production. Moreover, while it is often suggested that N from fossil fuel combustion sources is depleted in $^{15}N$ relative to precipitation, there is little evidence of a difference between the $\delta^{15}N$ of N from precipitation in clean and polluted areas (e.g., Heaton 1986). However, this second mechanism does not depend upon an isotopically distinct source of N from fossil fuel sources; observed values for NO$_3^-$ in deposition are lower than pre-industrial $\delta^{15}N$ values observed from bulk sediments and as such, increased deposition of N could lead to the observed $\delta^{15}N$ depletion without a distinct isotopic signature simply.

Fig. 4. Summary plot showing the temporal relationship between ice core NO$_3^-$ and $\delta^{15}N$ and sediment $\delta^{15}N$ and trends in pigment-inferred decline in N-fixing algae in two coastal lakes. Two upper most profiles: ice core NO$_3^-$ and $\delta^{15}N$ (data from Holtgrieve et al. 2011); lower central are centered values of $\delta^{15}N$ from the three lakes at the coast with significant declines in $\delta^{15}N$ (see Fig. 3). The fitted smooth (red line) is the result of a generalized additive model (GAM) fitted to the original, noncentered $\delta^{15}N$ values. The lowermost profiles are pigment ratios for three coastal lakes (AT1, AT6, and AT7) illustrating the relative change in the abundance of canthaxanthin (calculated as the ratio of canthaxanthin to diatoxanthin and alloxanthin concentrations; see Supporting Information) as a decline in potentially N-fixing cyanobacteria as the atmospheric N-load increases. The lack of change at AT7 is discussed in the main text. [Color figure can be viewed at wileyonlinelibrary.com]
by virtue of increasing proportions of this relatively light source of N.

Trophic interactions influence the fractionation of N and hence the δ15N record (France 2012) but the lakes in this study have short food chains (fish are present in only a few lakes) and their low productivity means input of organic debris from cladocerans, etc. is limited. Likewise, remains of aquatic higher plants, while present they are mainly limited to the littoral zone. Sediment cores were taken in the deepest part of the lakes where there is little, if any, in situ to the littoral zone. Sediment cores were taken in the deep-aquatic higher plants, while present they are mainly limited debris from cladocerans, etc. is limited. Likewise, remains of study have short food chains (fish are present in only a few

Another factor that might be amplifying 15N depletion in the relative importance of fossil fuel sources of NO3- to the total in-lake N pool at this location; the annual N flux relative to water column N pool is greatest at the coast (Table 1). Another factor that might be amplifying 15N depletion in the coastal lakes is that they are more hydrologically flushed [open] systems. Compared to the long retention time of the inland and ice margin lakes, where all inputs must be internally recycled and hence not fractionated, coastal lakes can lose NO3- through surface outflows. Osburn et al. (2017) recently highlighted the importance of hydrological linkage for DOC quality in coastal lakes. Further support for a hydrological component comes from the strong relationship between the high DOC concentration and organic N in the long-retention time lakes of the inland area (Anderson and Stedmon 2007).

Direct NO3- deposition as a proportion of the in-lake pool is greatest at the coast (Table 1), a detailed study of catchment snowpack (Curtis et al. 2018) found that sublimation and/or wind redistribution of snow resulted in an enhanced gradient from ice sheet to coast in terms of SWEs sitting on the lake ice, from 9–41 mm at the ice sheet and 43–53 mm at inland sites to 91–139 mm at the coast. Hence NO3 in the snowpack sitting on lake ice is at least 3.7× greater at the coast than inland, when expressed as a proportion of the lake TN pool. Coastal sites showing sediment δ15N depletion signals (AT1, AT6) have 2–5× more NO3- in lake snowpack (as a proportion of the lake TN pool; Table 1) than the only coastal site (AT7) which does not show δ15N depletion. Coastal site AT7 is more similar to those inland sites that show no trend in δ15N, in terms of the lake ice snowpack contribution to the TN pool. This site has a much greater in-lake NO3- concentration than other coastal lakes (Table 1) which means that the ratio of inputs to lake TN pool is much smaller (Table 1).

The recent (post-1996) upturn in sediment δ15N seen at AT6 and AT7 must either reflect a change in dominant atmospheric N sources (e.g., from fossil fuel and agriculture; cf. the ice core nitrate reported in Hastings et al. 2009) or the presence of diagenetic effects and perhaps differing sedimentation rates (see below). Ice core records show a clear decrease in fossil-fuel derived sulfate since around 1980 AD which is not so apparent in NO3-, potentially derived from other nonfuel sources which are increasing as fossil fuel emissions decrease (Fischer et al. 1998; Geng et al. 2014). When comparing the similar NO3- deposition to the whole catchment (i.e., maximum possible input) relative to the lake TN pools (both c. 13% per year) (Table 1) at AT1 (δ15N decline) and AT7 (no δ15N decline), the differing δ15N profiles cannot be explained. It is speculated that the presence of a morainic wetland upstream of AT7 is very likely attenuating the atmospheric NO3- signal conveyed to the downstream lake. There are also small lakes/ponds feeding AT7, which together with the wetland may increase catchment retention.

Limnological controls

There are number of aspects of the limnological gradients in the Kangerlussuaq study region that are relevant to the
discussion of N-cycling: the TN pool, NO$_3^-$ seasonality, nutrient limitation, and vertical stratification with associated bottom-water anoxia. Limnologically, the inland lakes are the most distinct with high DOC and conductivity (Table 2), hypolimnetic anoxia is common and there is a greater total in-lake N pool (TN $>$ 900 $\mu$g L$^{-1}$) compared to the coastal lakes ($<$ 300 $\mu$g L$^{-1}$). Much of the TN in the inland lakes is organic N (correlation of DOC and TN: $r = 0.78$; see Anderson and Stedmon 2007); in August 2001, $>$ 95% of the TN pool was in organic form (Anderson unpubl. data). Importantly, the inland lakes have a much lower atmospheric input of less depleted $^{15}$N (Fig. 2) but also have substantially longer retention times (Leng and Anderson 2003) which allows for microbial processing of the in-lake N pool. This greater recycling in the Inland region may account for the uniform $^{15}$N in the sediment profiles of these lakes (Fig. 3) (McCarthy et al. 2007).

Although the ice sheet margin and coastal lakes do not differ in terms of conductivity and hypolimnetic O$_2$ availability (Table 2) (see Whiteford et al. 2016 for details), there are significant differences in NO$_3^-$ concentration, which is greater in coastal lakes and rarely above detection limits at inland and ice margin sites. However, there was also seasonal variability across the region with maximum lake water NO$_3^-$ concentration recorded under ice or immediately after ice-out. Seasonally, nutrient limitation of phytoplankton yield differed significantly among sampling occasions; there were more occurrences of P-limitation under ice. Regional and seasonal variations in nutrient limitation status are linked to patterns of atmospheric Nr delivery and recycling of organic N under ice. Lowest rates of Nr delivery close to the ice sheet margin (Fig. 2), combined with elevated P inputs (via glacially derived dust) (Pulido-Villena et al. 2008; Bullard and Austin 2011; Hawkin et al. 2016) likely drive an imbalance in phytoplankton N : P stoichiometry (Table 2), generating increased growth-led demand for N. At the coast, where increased delivery of Nr accumulated in winter snowpack is released to lakes upon thaw, the N : P stoichiometric imbalance drives an increased demand for P (as recorded in spring under ice cover).

As many Arctic lakes are oligotrophic, low resource systems, where production is tightly controlled by nutrient supply (Bonilla et al. 2005), any increase in nutrient (e.g., Nr) supply could have a marked impact on phototrophic growth, stimulating primary production and impacting whole lake ecological structure and function. One adaptation to N scarcity in Arctic lakes (as with Arctic terrestrial ecosystems), is the abundance of N-fixing organisms (e.g., some cyanobacteria, lichens) which play a crucial role in alleviating ecosystem N-limitation. Nostoc are common in lakes throughout the study region, but particularly so in the central and ice marginal lakes and contain large amounts of the carotenoid canthaxanthin. Some indication of the increased N supply to the coastal lakes is provided by decreases in the relative abundance of canthaxanthin, a pigment associated with potentially $N_2$-fixing cyanobacteria in the coastal lakes AT6 and AT1, over the past $>$ 100 yr (Fig. 4; see also Supporting Information Fig. S14). This decrease (which mirrors changes in the ice core NO$_3^-$ concentration and coastal lake sediment $^{15}$N) suggests that an increased input of Nr helped to alleviate N-limitation in diatoms and cryptophytes or reduced the competitive benefits associated with N-fixation. At lake AT7, the low relative abundance of canthaxanthin (compared to AT1 and AT6) and absence of a depletion signal in the $^{15}$N profile are consistent with less N-limitation at this site; the lake has the highest NO$_3^-$ concentration of any lake in the study (Table 1). The lack of change in the pigment ratio over the last 150 yr at AT7 together with high total carotenoid concentrations would suggest that this lake has always had abundant and higher than average algal production. The local NO$_3^-$ source is unknown but is presumably derived from a wetland/glacial deposit located in its catchment.

**Anoxia and diagenesis**

Diagenesis can lead to marked changes in the isotopic values of nitrogen in organic matter post deposition (Talbot 2001). Most often this occurs in anoxic environments which result in denitrification, although other processes are known to affect isotopic values (Teranes and Bernasconi 2000; Burkin and Hamilton 2007). The anaerobic processes of denitrification and ammonification both heavily discriminate against $^{15}$N resulting in enrichment of the DIN reservoir and consequently also of subsequently derived organic matter (Wolfe et al. 1999; Olsen et al. 2013). If these processes (ammonification and denitrification) were dominant, the resultant $^{15}$N values should be higher than the $^{15}$N observed values in the inland lakes where anoxia is prevalent. Interestingly, the geographic pattern in regional $^{15}$N profiles does not correspond with limnological O$_2$ gradients: the lakes with the lowest hypolimnetic O$_2$ concentrations (the inland cluster) have the most stable $^{15}$N profiles (Fig. 3) while the coastal and ice margin lakes which have differing $^{15}$N profiles have similar hypolimnetic O$_2$ concentrations (see Whiteford et al. 2016).

Some indication of the role played by limnology and anoxia in $^{15}$N processing are, however, shown by the two adjacent lakes on a nunatak at the ice margin and SS16 (see Anderson et al. 2001) (Fig. 3, insets). These lakes differ in terms of their thermal stratification and chemical characteristics (Anderson et al. 2001) and the $^{15}$N profiles are different (Fig. 3, inset). The strong positive trend in $^{15}$N at SS86 may be associated with changing abundance of phototrophic bacteria (Reuss et al. 2013). In contrast, at SS1220 (an inland lake) where changing strength of long-term thermal stratification was inferred from geochemical proxies (Olsen et al. 2013), the fluctuations between strong and weak thermal stratification (and hence O$_2$ availability) did not show in the $^{15}$N record.
If all available N from the DIN pool is assimilated by algae, the δ15N of the algal component as being driven by changes in N delivery, i.e., a shift in N cycling caused by increasing anthropogenic N. They also suggest that diagenetic effects are less than the fingerprint of regional changes in N biogeochemistry, so that bulk sediments reflect the signal of the 15N inputs, i.e., diagenetic effects in the sediment are minor. The generally low sediment δ15N values (1–2‰) at the inland and ice margin lakes suggest that the organic matter may be derived from cyanobacteria fixing atmospheric nitrogen (~ 0‰) (Talbot 2001). Sobek et al. (2014) found a strong correlation between the sediment δ15N value and O2 exposure time in a group of Greenland lakes, with δ15N increasing from 0.5‰ to +3‰, as O2 exposure increased from ~ 2 yr to > 10 yr. The O2 exposure of organic matter is largely controlled by the sediment accumulation rate and the O2 content of the hypolimnion, suggesting that more positive δ15N values should be found in lakes with slow sediment accumulation rates and oxic hypolimnion (i.e., Coastal and Ice Margin). Two coastal lakes (AT6, AT7) show a positive upturn in δ15N values around the year ~ 2000 AD and it is possible that this is the result of greater O2 penetration (cf. Sobek et al. 2014), perhaps associated with changed thermal stratification patterns (Saros et al. 2016). Some further support for a recent diagenetic signal at AT7 is suggested by the pigment profiles which indicate changed preservation conditions at this time (~ 2000 AD). Today, this lake has highly oxygenated bottom waters, presumably due to abundant macrophytes in the littoral zone.

**Landscape perspective**

The response of lake nitrogen (N) biogeochemistry to catchment vegetation and soil dynamics change is complex (Baron et al. 2013). Mineralized N is frequently a limiting nutrient in Arctic ecosystems (Dormann and Woodin 2002), the fate of which is key to understanding changes in the availability of nutrients to catchment vegetation and lake biota. Where the permafrost underlying tundra has started to thaw (e.g., North Slope of Alaska) (McClelland et al. 2007; Harms and Ludwig 2016; Harms et al. 2016), there have been dramatic changes in nutrient soil water interactions. Deepening of the active layer leads to enhanced soil organic matter decomposition rates and consequently to greater N mineralization. This increases the local supply of N that occurs during spring thaw, resulting in a temporal mismatch between availability and biological uptake, thereby enhancing availability for leaching into surface waters during snow melt. However, Bartrons et al. (2010) showed how soil type in a catchment contributes to higher δ15N than that related to snow melt processes, which may reflect local soil dynamics and vegetation effects. Increased decomposition rates associated with warming and/or vegetation changes are also reflected in higher δ15N in soil organic matter and consequently in NO3 leached from soils to lakes, which may be recorded in lake sediments. However, Kangerlussuaq was cooling for much of the 20th century (Mernild et al. 2014) and there is also limited hydrological connectivity at the inland and ice margin sites. In the Kangerlussuaq area of SW Greenland, the thickest organic soils are located close to the head of the fjord associated with the dwarf shrub tundra, while there is clearly more biological processing of terrestrial organic matter in this location, there are few hydrological pathways for soil and vegetation isotopic signatures to be transported into the lakes. As a result, catchment soils and vegetation have minimal influence on the δ15N in these lakes. At the ice margin, the vegetation is also sparse (predominantly steppe) with the result that soils are thin; there are also large areas of bare ground due to the inhospitable climate, wind speeds can be very high. Importantly, however, here too, hydrological connectivity is limited. Snow sublimation is a major factor at both the inland and ice margin sites which influences the snowpack δ15N and lake hydrologic budgets.

The coastal catchments also have limited vegetation cover (at altitudes > 400 m they resemble high Arctic systems): soils are thin or absent. Total precipitation and snow cover are also substantially higher (see above) and while hydrological connectivity is much greater compared to the inland sites, the thin soils suggest that catchment processing of N is limited, with the exception of the AT7 catchment (see above; Table 1).

At the coast, atmospheric deposition inputs of DIN, whether in spring snowmelt or annual deposition load (Fig. 2), proportionately represent a much greater fraction of the inflake pool of TN (Table 1). Rapid hydrological transfer means that the isotopic signature of the atmospherically derived NO3 is delivered to a much less modified N pool and captured by in-lake production and then sedimented in the lake. Furthermore, coastal deposition is much more depleted in 15N than inland (Fig. 2). The rapid hydrological transfer means that there is limited microbial processing (and hence isotopic fractionation) (Finlay et al. 2007). Theoretically, the total atmospheric NO3 deposition flux to an entire lake catchment defines the total potential load (or an upper limit) for NO3 which may be transported into a lake. Here, the relationship to lake TN pools is more complex. At the coastal sites, there is an order of magnitude more NO3 deposited onto catchments relative to lake TN pools, with NO3 deposition averaging ~ 18% of lake TN pools per annum, compared with <2% inland (Table 1). At site AT6, annual catchment NO3 deposition is equivalent to >30% of the lake TN pool. If deposited nitrate were completely mobile, then an atmospheric deposition source would...
account for a third of the lake TN pool each year. However, it is known that terrestrial Arctic systems strongly retain N inputs and only a fraction of deposited NO$_3^-$ is likely to reach lakes (Tye et al. 2005). This proportion must though be largest at the coast where precipitation is much higher and surface flow pathways are much more pronounced. If spring snowpack inputs to lakes reflect the dominant atmospheric source, then the signal should be much more apparent in coastal lakes. Likewise, annual deposition to the whole catchment is much greater at the coast, where the conditions for surface runoff inputs to lakes outside of the snow season are also greatest. Hence, although it is not possible to precisely quantify the proportion of catchment snowmelt or annual deposition that is transported into lakes to be utilized for primary production, all the evidence indicates that the coastal sites showing clear sediment $\delta^{15}$N signals are those experiencing the greatest deposition inputs, and where atmospheric nitrate also has the lowest $\delta^{15}$N values (Fig. 2; Table 1). The lack of a signal in AT7 is not due to lower snowpack or deposition inputs, but rather due to the larger lake TN pool and possible processing of catchment N inputs in an upstream wetland which is unique to this site within the current study.

Synthesis

The majority of lakes analyzed for sediment $\delta^{15}$N along the regional N deposition gradient in SW Greenland show little agreement with the ice core records of altered atmospheric N dynamics (both quality and total amount) (Hastings et al. 2009; Holtgrieve et al. 2011). This lack of a signal, of course, does not preclude ecological effects driven by N-deposition in this area, merely that there is no sediment $\delta^{15}$N record of the increased deposition. In contrast, most coastal lakes show the characteristic decline of $\sim 1$–1.5‰ in $\delta^{15}$N over the last 100–130 yr that has been observed in selected northern hemisphere lakes (Holtgrieve et al. 2011). The differences in historic $\delta^{15}$N sediment records observed in this study (over a 170 km transect) cannot be readily explained by limnological processes and/or diagenesis but most likely reflects the interplay between the atmospheric N-load, the more depleted isotopic signature at the coast, N processing in the snow pack and the size of the in-lake N pool. At coastal sites, the rapid incorporation of the isotopically negative, reactive N into organic matter and transfer to the sediment provides an unambiguous record of changing N dynamics in the coastal region. Hobbs et al. (2016) found that the relationship between sediment $\delta^{14}$N and measured atmospheric deposition relies on catchment N retention. Given the observations in this study and those elsewhere (Curtis and Simpson 2011) variable $\delta^{14}$N signals are probably the norm and that only lakes and catchments with certain characteristics will record the atmospheric depletion signal. Although the N-load is low in SW Greenland (< 0.5 kg ha$^{-1}$ yr$^{-1}$), sustained inputs are sufficient to alter the $\delta^{15}$N signal (and drive ecological change) if the recipient lakes are oligotrophic and sensitive to external forcing having developed under low background N deposition loads.

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Conflict of Interest
None declared.