

# Changing nitrogen deposition with low $\delta^{15}\text{N}-\text{NH}_4^+$ and $\delta^{15}\text{N}-\text{NO}_3^-$ values at the Experimental Lakes Area, northwestern Ontario, Canada

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## Abstract

Ammonium deposition at the International Institute for Sustainable Development Experimental Lakes Area (IISD-ELA), in northwestern Ontario, Canada, has doubled in the last 45 years and thus is no longer among the low nitrogen (N) deposition sites in North America. This may be related to the concurrent intensification of Manitoba agriculture to the west and upwind of the ELA. Large increases in ammonium deposition at the ELA were important in driving the observed trend and increased the  $\text{NH}_4^+$  to  $\text{NO}_3^-$  ratio of input to aquatic and terrestrial systems. Stable isotope analyses of two years of bulk (wet and dry) atmospheric deposition revealed very large ranges in  $\delta^{15}\text{N}-\text{NH}_4^+$  (22‰ range),  $\delta^{15}\text{N}-\text{NO}_3^-$  (18‰), and  $\delta^{18}\text{O}-\text{NO}_3^-$  (19‰). Few other  $\delta^{15}\text{N}-\text{NH}_4^+$ ,  $\delta^{15}\text{N}-\text{NO}_3^-$ , and  $\delta^{18}\text{O}-\text{NO}_3^-$  values have been published for Canadian precipitation. Increases in  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in July occurred with increases in total N deposition. The wide range and seasonal trends of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values in ELA precipitation mean that studies characterizing N inputs to watersheds and lakes require an ongoing and comprehensive annual sampling regime. Global trends of declining  $\delta^{15}\text{N}$  of N deposition evident in lake sediment records may be a result of increases in  $\text{NH}_4^+$  deposition with lower  $\delta^{15}\text{N}-\text{NH}_4^+$  values. Similarly, the relationship in Lake Superior between increasing  $\text{NO}_3^-$  and lower  $\delta^{15}\text{N}-\text{NO}_3^-$  values may be explained by increased atmospheric deposition of N with low  $\delta^{15}\text{N}$  values.

**Key words:** nitrogen, precipitation, ammonia, nitrate, isotope

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## Introduction

Release of nitrogen (N) to the atmosphere has been increasing globally due to greater emissions of N from human activities (Vitousek et al. 1997; Galloway et al. 2003, 2004). These N emissions react to form N species that are deposited onto ecosystems hundreds of kilometres from the source (Asman et al. 1998). Nitrogen deposition is one component in the calculation of critical loads for acid sensitive lakes and soils (Schulze et al. 1989; Driscoll et al. 2001; Jeffries et al. 2003). Although N is often a limiting element for forest growth, the loss of base cations from soils as a result of oxidized N loading can compromise forest response to N fertilization. At elevated levels of N deposition, forest productivity and biomass decrease, whereas emissions of the potent greenhouse gas, nitrous oxide, increase (Aber et al. 1989; Matson et al. 2002; Venterea et al. 2003). Global N deposition modeling indicates

that 50–80% of N deposition falls on natural (non-agricultural) areas and N accumulation is driving changes in terrestrial plant diversity (Dentener et al. 2006; Bobbink et al. 2010).

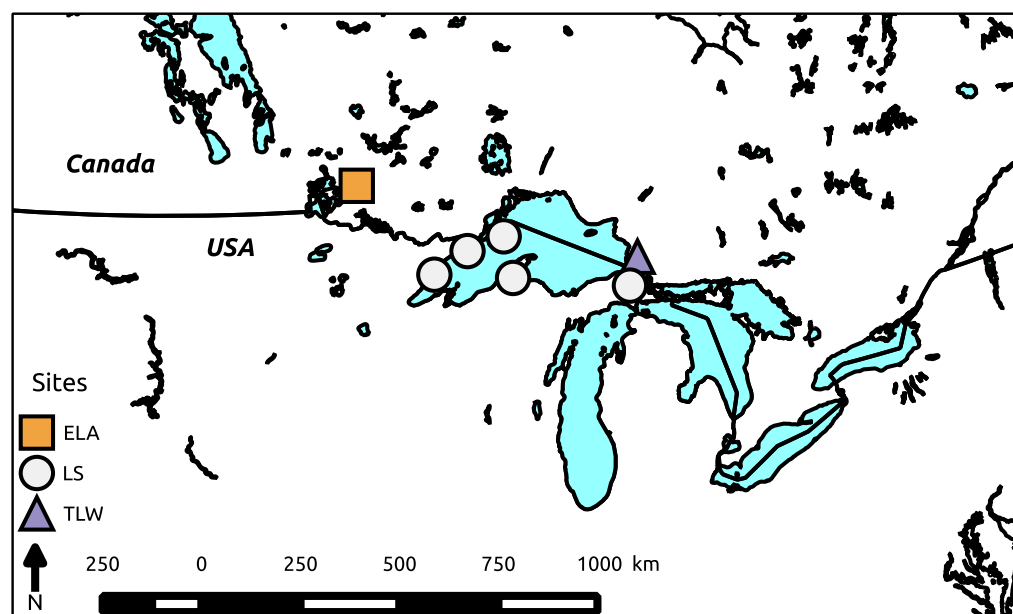
Natural abundance stable isotope ratios of N and oxygen (O) ( $^{15}\text{N}/^{14}\text{N}$ , hereafter  $\delta^{15}\text{N}$ ; similarly  $^{18}\text{O}/^{16}\text{O}$ , hereafter  $\delta^{18}\text{O}$ ) are used to determine the proportion of atmospheric N that is incorporated into ecosystems and to separate new from old N sources (e.g., Kendall 1998; Mayer et al. 2001; Spoelstra et al. 2007). Atmospheric processes involving N species have also been inferred from the observed changes in stable isotope composition of N deposition including temperature (Freyer et al. 1993),  $\text{NO}_x$  source, storm track (Buda and DeWalle 2009), duration of rain event (Buda and DeWalle 2009), temporal separation from previous rain events (Heaton 1987), halogen chemistry (Altieri et al. 2013), and atmospheric chemical reactions of  $\text{NO}_3^-$  precursors (Freyer et al. 1993; Michalski et al. 2012).

There are few studies on atmospheric  $\text{NO}_3^-$  isotopes in Canada (Mayer et al. 2001; Spoelstra 2004; Spoelstra et al. 2001, 2004, 2007, 2010). Most published  $\delta^{15}\text{N}$ – $\text{NO}_3^-$  data are from heavily impacted systems in Europe, the eastern USA, northern Europe, and China (e.g., Hastings et al. 2003; Elliott et al. 2007, 2009; Zhang et al. 2008; Fang et al. 2011; Koszelnik and Gruca-Rokosz 2013; Korth et al. 2014; Yang et al. 2014; Guerrieri et al. 2015; Yu et al. 2016). In general, fewer studies with  $\text{NH}_4^+$  isotopes in atmospheric deposition are available (e.g., Garten 1992; Zhang et al. 2008). Recently, Holtgrieve et al. (2011) suggested that by more than doubling the reactive N in the biosphere and increasing atmospheric  $\text{CO}_2$  concentration, the  $\delta^{15}\text{N}$  of lake sediment has been altered. Even in remote areas, the deposition of N species and their associated  $\delta^{15}\text{N}$  values have changed (Dentener et al. 2006; Knapp et al. 2008, 2010) and lake sediments have recorded a decrease in  $\delta^{15}\text{N}$  over the last century (Wolfe et al. 2003; Hobbs et al. 2010; Holtgrieve et al. 2011).

Here, we examine trends in N deposition and the stable isotopic values of N species at a site remote from urban and agricultural activities. The IISD–Experimental Lakes Area (ELA) in northwestern Ontario, Canada, has been the site of long-term whole-ecosystem research for over 45 years (Blanchfield et al. 2009). Nitrogen deposition at the ELA is currently less than one third that of the most impacted sites in eastern North America and Europe (Watmough et al. 2005; Pardo et al. 2011). Our objectives in this paper are to (1) assess annual and open water season changes in the speciation of atmospheric N deposition at the ELA over 44 years of record; (2) characterize the seasonal variability in  $\delta^{15}\text{N}$ – $\text{NO}_3^-$ ,  $\delta^{18}\text{O}$ – $\text{NO}_3^-$ ,  $\delta^{15}\text{N}$ – $\text{NH}_4^+$ , and  $\delta^{15}\text{N}$ –total nitrogen (TN) of atmospheric deposition at the ELA; and (3) compare these values with dissolved organic matter (DOM), particulate organic matter (POM), and zooplankton at the base of ELA food webs.

## Methods

The ELA is situated on the Canadian Shield in the boreal forest of northwestern Ontario, Canada ( $93^\circ 41' \text{W}$   $49^\circ 41' \text{N}$ ; Fig. 1). The ELA climate is continental with cold winters and warm summers. Average annual precipitation is 707 mm/year (1970–2013). Climate and deposition measurements, including chemistry, have been made in the Lake 239 catchment since June 1969. In the early 1970s, N deposition at the ELA was among the lowest recorded in North America; however, this is no longer the case (Parker et al. 2009). Bulk deposition was collected during the ice-free season at the Lake 239 island from 1969 to 1983 before being moved to the nearby Lake 240 island. There is no evidence indicating that the change in location affected the data. Precipitation has also been collected at the ELA Meteorological Station since 1970. Detailed methods are outlined by Beaty (1981) and Linsey et al. (1987). Briefly, in summer,  $0.5 \text{ m} \times 0.5 \text{ m}$  plexiglass bulk deposition collectors for wet and dry deposition screened to  $100 \mu\text{m}$  were emptied after enough water was collected for analyses, filtered, and stored cold until chemical analyses were performed within a few days. In winter, snow from the collector was pushed with a clean paddle into a plastic bag and kept frozen until analysis.



**Fig. 1.** Map of North America showing the Environmental Lakes area (ELA) study location and nearby sites with comparable data sets: Turkey Lakes Watershed (TLW) and Lake Superior (LS). Made with Natural Earth (free vector and raster map data available from [www.naturalearthdata.com](http://www.naturalearthdata.com)).

Bulk deposition samples for isotopic analyses were collected at the meteorological site in a collector from 6 June 2012 to 21 March 2013. Samples from a bulk collector in the Lake 302 catchment, about 3 km away, collected from April to September 1996, were archived frozen (as per Lamontagne and Schiff 1999) and analysed for this study.

Stream and lake survey samples of DOM, POM, and zooplankton were collected from the epilimnion of eight lakes (114, 239, 303, 304, 737, 626, 658, and 979) and five streams (water only) at the ELA (Lake 114 inflow, Lake 114 cliff inflow, Lake 240 inflow from Lake 470, Lake 302 upland 8, and Lake 979 east inflow) in mid-July 2010 (except Lake 114 inflow samples, which were collected during the summers of 2000–2002). Water samples were filtered with pre-combusted QMA filters (nominal pore size of 0.8  $\mu\text{m}$ ). Filtrate was acidified with concentrated HCl to pH 4 before being freeze-dried. Zooplankton were collected by towing a 50 cm diameter net with a 150  $\mu\text{m}$  mesh behind a boat. Samples were washed and freeze-dried. Both freeze-dried material and filters were analysed for  $\delta^{15}\text{N}$  on a Carlo Erba 1108 elemental analyser coupled to a Thermo Finnigan Delta<sup>+</sup> continuous flow isotope-ratio mass spectrometer (EA-IRMS).

ELA deposition samples were analysed by standard methods (Stainton et al. 1977).  $\text{NO}_2^-$  was analysed colorimetrically by the azo dye method on a Technicon Autoanalyzer.  $\text{NO}_3^-$  was analysed colorimetrically following reduction to  $\text{NO}_2^-$  via a copper-cadmium couple by the azo dye method on a Technicon Autoanalyzer.  $\text{NH}_4^+$  was analysed colorimetrically by the indophenol blue method with nitroprusside catalyst on a Technicon Autoanalyzer. Total dissolved nitrogen (TDN) was analysed by photo-oxidation of alkaline samples, and the subsequent  $\text{NO}_3^-$  was reduced to  $\text{NH}_4^+$  by zinc in acid, then analysed colorimetrically as per  $\text{NH}_4^+$ . Dissolved organic nitrogen (DON) was calculated as the difference between TDN and the sum of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ . Prior to 1989,  $\text{NO}_2^-$  was not reported separately from  $\text{NO}_3^-$  and the values reported

here for  $\text{NO}_3^-$  include  $\text{NO}_2^-$ . After 1989, we used only the  $\text{NO}_3^-$  values.  $\text{NO}_2^-$  values in bulk collected deposition are very small, averaging 1.4% of total  $\text{NO}_3^- + \text{NO}_2^-$  from 1990 to 2013.  $\text{NO}_2^-$  is included in the TN and TDN analyses in the entire data record. Suspended N was collected by filtration on a glass fibre filter and analysed on an elemental analyser.

Bulk deposition samples in 2010–2012 were collected at the ELA meteorological site in plastic bags in about two week intervals. Bags were sealed, kept cold, screened to 150  $\mu\text{m}$ , transferred to Nalgene bottles, and frozen within 2 d. Samples were kept frozen until analysis. Bulk deposition samples at the Lake 302 uplands were collected in 1996 on a storm event basis and were treated similarly.

For isotopic analysis,  $\text{NO}_3^- + \text{NO}_2^-$  concentrations were determined using a Westco SmartChem 200 discrete analyzer with a method based on [USEPA 353.2 Revision 2.0 \(1993\)](#).  $\text{NO}_3^-$  was reduced to  $\text{NO}_2^-$  by passage of the sample through a tubular copperized cadmium reactor from which  $\text{NO}_2^-$  was treated with sulphanilamide and N-(naphthyl)-ethylenediamine dihydrochloride to form a dye measured colorimetrically at 550 nm. Precision was  $\pm 0.02$  mgN/L.  $\text{NH}_4^+$  concentrations were analysed manually using spectrophotometer on unfiltered samples.  $\text{NH}_4^+$  was reacted with alkaline phenol and then hypochlorite-forming indophenol blue, which was intensified by adding sodium nitroprusside before analysis at 600 nm. Precision was  $\pm 0.08$  mgN/L.

For  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  analysis,  $\text{NO}_3^- + \text{NO}_2^-$  was chemically reduced to  $\text{N}_2\text{O}$  ([McIlvin and Altabet 2005](#)). Briefly,  $\text{NO}_3^-$  was reduced to  $\text{NO}_2^-$  with cadmium and then  $\text{NO}_3^- + \text{NO}_2^-$  was reduced to  $\text{N}_2\text{O}$  with  $\text{NaN}_3$ .  $\text{N}_2\text{O}$  was analysed with a VG IsoPrime continuous flow isotope-ratio mass spectrometer with a VG TraceGas pre-concentrator. Analyses were performed in duplicate. Precisions were  $\pm 0.2\text{‰}$  for  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\pm 0.5\text{‰}$  for  $\delta^{18}\text{O}-\text{NO}_3^-$ .

For  $\delta^{15}\text{N}-\text{NH}_4^+$  analysis,  $\text{NH}_4^+$  was chemically converted to  $\text{N}_2\text{O}$  ([Zhang et al. 2007](#)). Briefly,  $\text{NH}_4^+$  was oxidized to  $\text{NO}_2^-$  with  $\text{BrO}^-$  and then reduced to  $\text{N}_2\text{O}$  with  $\text{NaN}_3$ . The resulting  $\text{N}_2\text{O}$  was analysed as above in duplicate. Precision was  $\pm 0.3\text{‰}$ .

For  $\delta^{15}\text{N}-\text{TN}$  analysis, sample volumes were reduced by evaporation from about 2 L to about 100 mL. Samples were freeze-dried and packed into tin cups for analysis on the EA-IRMS as above. Precision was  $\pm 0.3\text{‰}$ .

Concentrations and precipitation depths were combined to yield areal deposition rates on an annual basis and for the open water season of late-April to the end of September (ice-off to thermal destratification, d 120–273). There are a few external inputs of N to these small headwater lakes other than atmospheric deposition once they are thermally stratified and after snowmelt. Long-term trends were assessed with the non-parametric Mann–Kendall test ([McLeod 2011](#)) in R ([R Core Team 2016](#)).

## Results

### Historical precipitation and N deposition at the ELA

Annual and open water season precipitation at the ELA varied by a factor of two over the 44 year historical record ([Fig. S1](#)). Average annual precipitation was 707 mm (1970–2013) and in 2010–2012, the years with samples collected for detailed isotopic analyses, precipitation amounts of 955, 660, and 670 mm were recorded. In the open water season when there is the greatest primary production (e.g., [Fee 1976](#)), average precipitation over 44 years was 453 mm and in 2010–2012, 734, 451, and 356 mm were received. Precipitation was lower in the 1980s than in recent decades and year-to-year variability was often large. The calendar year and open water season of 2010 were among the 10 wettest in the ELA record.

Over the 44 year record,  $\text{NO}_3^-$  deposition at the ELA exhibited no appreciable change, whereas  $\text{NH}_4^+$  deposition has increased (Fig. 2 and Tables 1 and 2). The majority of the increase has occurred since 1980 (Fig. 2). Annual average  $\text{NH}_4^+$  concentrations increased from 269  $\mu\text{gN/L}$  in the first 10 years to 417  $\mu\text{gN/L}$  in the most recent 10 years (Fig. S2, top). Open water season volume-weighted TN concentrations remained constant over those intervals, 881 and 947  $\mu\text{gN/L}$  (Fig. S2, bottom). Increases in  $\text{NH}_4^+$  deposition were a result of increases in both concentrations and precipitation. There were weak, but significant, correlations between N deposition and precipitation (all  $r$  are 0.20–0.40; all  $p < 0.05$  except TDN).

As a result of increased  $\text{NH}_4^+$  deposition, the ratio of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  increased (Fig. 3). The average ratio of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  in the first 10 years of the record was 1.1 (1.2 in open water season) and in the last 10 years it was 1.6 (1.9 in open water season). Suspended N averaged 15% of TN deposition and was slightly lower in the 1980s.

### Concentration of $\text{NO}_3^-$ and $\text{NH}_4^+$ in deposition in 2010–2012

Deposition samples collected for isotopic analyses in 2010 and 2011–2012 represented 90% and 97%, respectively, of the total precipitation that fell during the sampling period. Non-volume-weighted  $\text{NH}_4^+$  concentrations were between 40 and 880  $\mu\text{gN/L}$  (average concentration 325  $\mu\text{gN/L}$ ) in 2010 and 2011–2012 and were similar to those of the last 10 years of the record (as above and Table 1). Non-volume-weighted  $\text{NO}_3^-$  concentrations were between 70 and 490  $\mu\text{gN/L}$  (average concentration 254  $\mu\text{gN/L}$ ) and did not vary as much as  $\text{NH}_4^+$ .

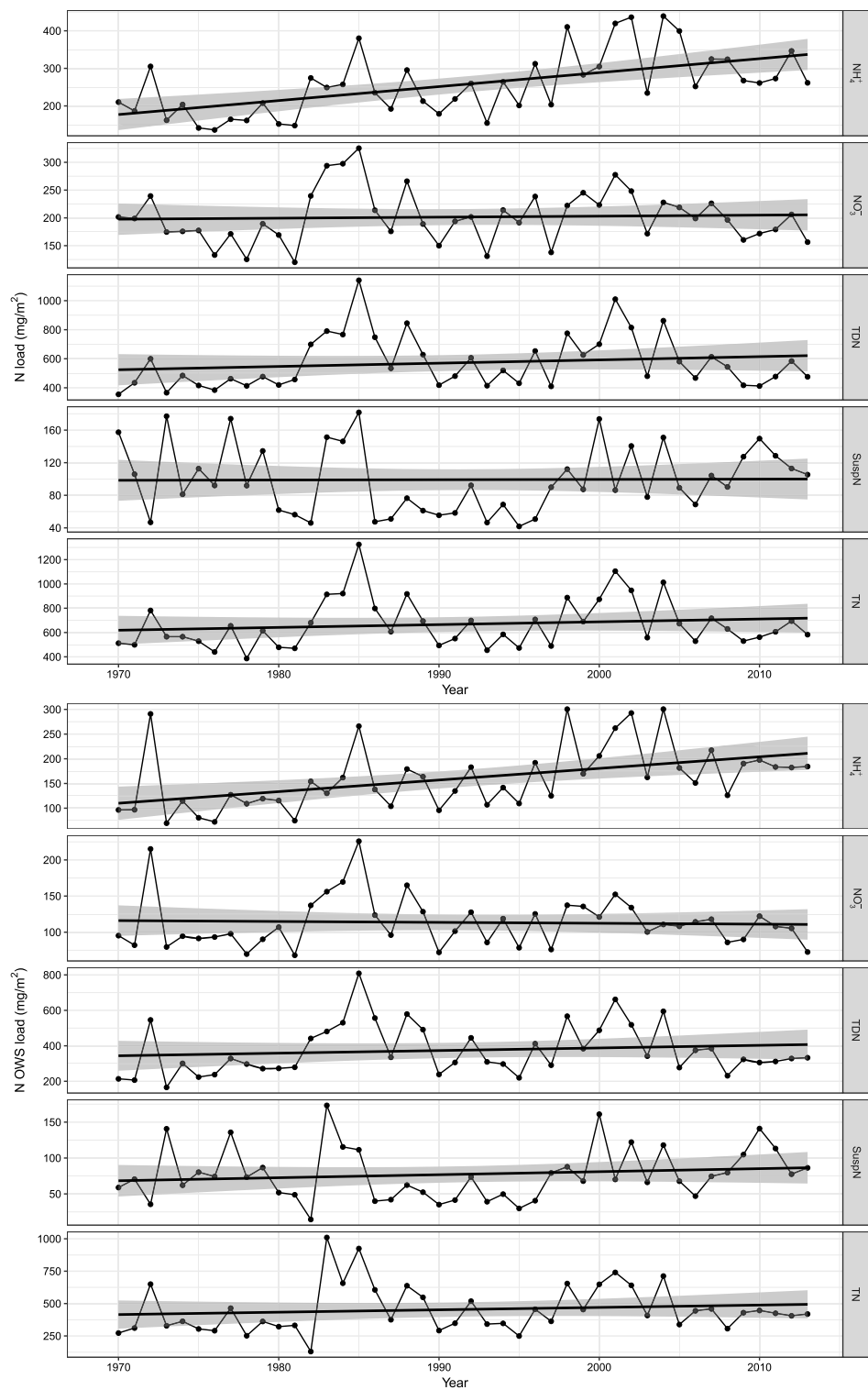
### Nitrogen and oxygen isotopes in atmospheric deposition

Published  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  values in atmospheric deposition from sites around the world, including urban, rural, and forested locations, exhibit a very large range:  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  ranges from  $-13\text{‰}$  to  $+5\text{‰}$  and  $+12\text{‰}$  to  $+86\text{‰}$ , averaging  $-3.0\text{‰} \pm 3.5\text{‰}$  and  $+65.0\text{‰} \pm 15.2\text{‰}$  (Figs. 4, S3). Values of  $\delta^{15}\text{N}-\text{NO}_3^-$  at the ELA varied from  $-12.0\text{‰}$  to  $+1.0\text{‰}$  in 2010–2012, with the lowest  $\delta^{15}\text{N}-\text{NO}_3^-$  values in spring (Fig. 5). Higher values in summer than winter were also observed at the Turkey Lakes Watershed (TLW) and around Lake Superior, Canada (Spoelstra et al. 2001; Spoelstra 2004; Finlay et al. 2007).

Values of  $\delta^{18}\text{O}-\text{NO}_3^-$  were greatest in winter and lowest in mid-summer (Fig. 5), ranging from  $+63\text{‰}$  to  $+82\text{‰}$  in 2010–2012. Both deposition and throughfall from 1996 also exhibit the same seasonal trend (highest values in winter, lowest in mid-summer), as did TLW (Spoelstra 2004), Huntington Forest in Adirondack Park, New York (Campbell et al. 2006), and mid-Appalachia, Pennsylvania and West Virginia (Williard et al. 2001).

TLW and the southern shore of Lake Superior are the closest sites to the ELA; TLW data show comparable  $\delta^{15}\text{N}-\text{NO}_3^-$  values but lower  $\delta^{18}\text{O}-\text{NO}_3^-$  values than the ELA (Spoelstra 2004) or the Lake Superior sites (Finlay et al. 2007) even though the measurements spanned more than a decade: 2000–2002 at TLW and 2004–2006 at Lake Superior, and 1996 and 2010–2012 at the ELA. Other more distant North American sites have similarly large ranges in  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  over the open water season (Williard et al. 2001; Burns and Kendall 2002; Campbell et al. 2006; Barnes et al. 2008). There were no relationships between  $\text{NO}_3^-$  concentrations and  $\delta^{15}\text{N}-\text{NO}_3^-$  or  $\delta^{18}\text{O}-\text{NO}_3^-$  values ( $r = -0.25$  and  $0.09$ ,  $p = 0.11$  and  $0.57$ ) at the ELA. Mass-weighted  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  values for deposition at the ELA for 2010–2012 were  $-4.4\text{‰}$  and  $+68.4\text{‰}$ , very close to the means of published values at  $-2.7\text{‰}$  and  $+64.3\text{‰}$ .

There are many factors that have been shown to influence the isotopic composition of  $\text{NO}_3^-$  including, but not limited to, temperature, UV radiation (Freyer et al. 1993),  $\text{NO}_x$  source, storm track



**Fig. 2.** Annual and open water season (OWS) nitrogen deposition at the Experimental Lakes Area for the period from 1970 to 2013. Grey bands are the 95% confidence intervals around the linear regressions. TDN, total dissolved nitrogen; SuspN, suspended nitrogen; TN, total nitrogen.



**Table 1.** Long-term annual means and trends for the period from 1970 to 2013 in N species in bulk atmospheric deposition at the Environmental Lakes Area (ELA).

	Volume-weighted mean concentration			Deposition		
	Mean	Trend	<i>p</i>	Mean	Trend	<i>p</i>
Ammonium	364	<i>4.29</i>	<i>&lt;0.001</i>	257	<i>3.72</i>	<i>&lt;0.001</i>
Nitrate	289	−0.436	0.708	201	0.181	0.649
Suspended N	140	−0.267	0.879	99	0.034	0.635
TDN	821	0.784	0.649	572	2.26	0.160
TN <sup>a</sup>	955	0.624	0.537	668	2.31	0.172
Precipitation	—	—	—	707	1.70	0.347

**Note:** Concentrations are in mgN/m<sup>3</sup>, deposition in mgN/m<sup>2</sup>, trends in mgN/(m<sup>3</sup>·year) and mgN/(m<sup>2</sup>·year), and precipitation in mm/year. *p*-values from Mann–Kendall trend analysis. Statistically significant trends (*p* < 0.05) are identified in italics. TDN, total dissolved nitrogen; TN, total nitrogen; SuspN, suspended nitrogen.

<sup>a</sup>TN = SuspN + TDN.

**Table 2.** Long-term open water season (May to October, inclusive) means and trends for the period from 1970 to 2013 in nitrogen species in bulk atmospheric deposition at the Environmental Lakes Area (ELA).

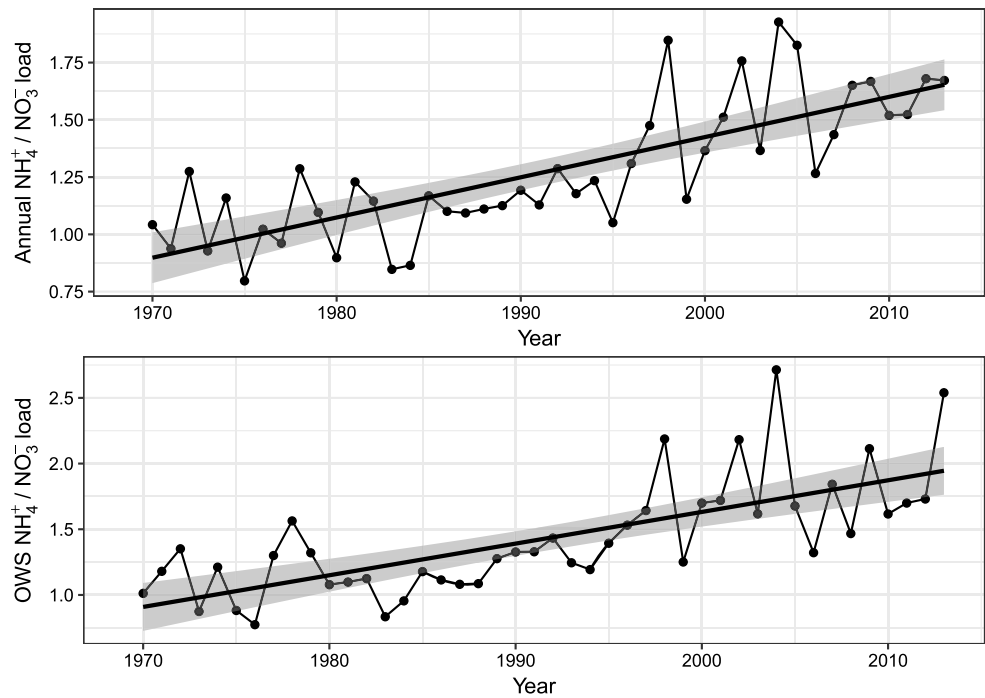
	Volume-weighted mean concentration			Deposition		
	Mean	Trend	<i>p</i>	Mean	Trend	<i>p</i>
Ammonium	359	<i>3.74</i>	<i>0.003</i>	161	<i>2.35</i>	<i>&lt;0.01</i>
Nitrate	261	−1.46	0.346	113	−0.124	0.769
Suspended N	177	−0.182	0.511	77	0.421	0.191
TDN	856	−0.507	0.847	375	1.47	0.091
TN <sup>a</sup>	1043	−1.00	0.472	454	1.83	0.137
Precipitation	—	—	—	453	2.02	0.206

**Note:** Mean concentrations are in mgN/m<sup>3</sup>, deposition in mgN/m<sup>2</sup>, trends in mgN/(m<sup>3</sup>·year) and mgN/(m<sup>2</sup>·year), and precipitation in mm/year. *p*-values from Mann–Kendall trend analysis. Statistically significant trends (*p* < 0.05) are identified in italics. TDN, total dissolved nitrogen; TN, total nitrogen; SuspN, suspended nitrogen.

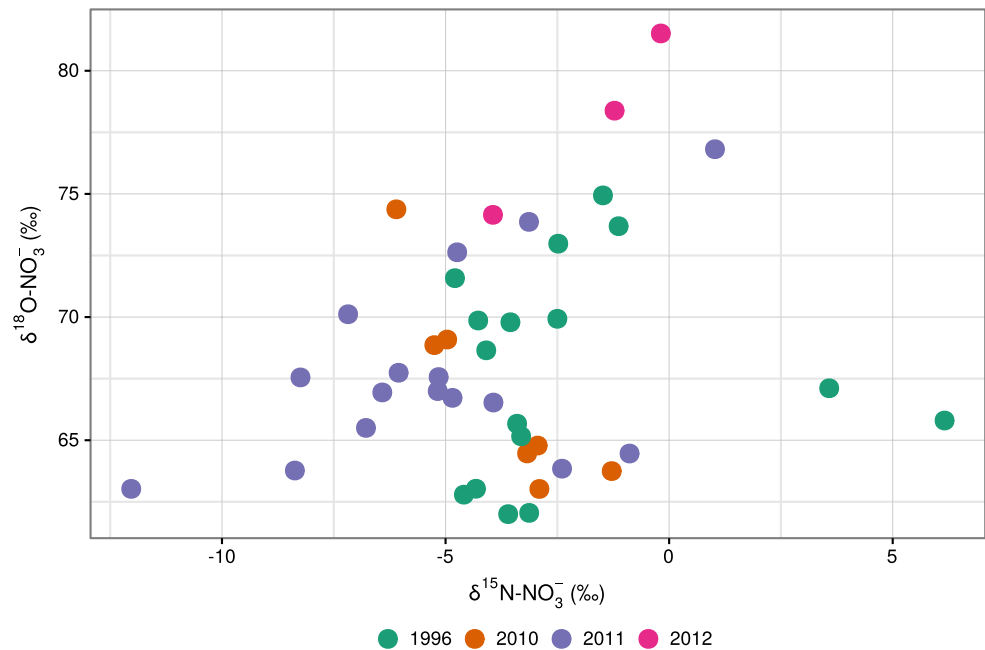
<sup>a</sup>TN = SuspN + TDN.

(Buda and DeWalle 2009), duration of rain event (Buda and DeWalle 2009), temporal separation from previous rain events (Heaton 1987), and atmospheric chemical reactions of NO<sub>3</sub><sup>−</sup> precursors (Freyer et al. 1993).

Published δ<sup>15</sup>N–NH<sub>4</sub><sup>+</sup> values average −6.4‰ ± 5.5‰ with a large total range from −21.8‰ to +5.7‰ (Fig. 5). There are no previously published δ<sup>15</sup>N–NH<sub>4</sub><sup>+</sup> values in Canada. At the ELA, δ<sup>15</sup>N–NH<sub>4</sub><sup>+</sup> values in 2010–2012 ranged from −20.8‰ to +1.1‰ with a mass-weighted mean of −7.4‰, lower than for δ<sup>15</sup>N–NO<sub>3</sub><sup>−</sup> (−4.4‰). Highest δ<sup>15</sup>N–NH<sub>4</sub><sup>+</sup> values were in the summer (Fig. 5). The δ<sup>15</sup>N–NH<sub>4</sub><sup>+</sup> values show no relationship with NH<sub>4</sub><sup>+</sup> concentration (*r* = 0.26,

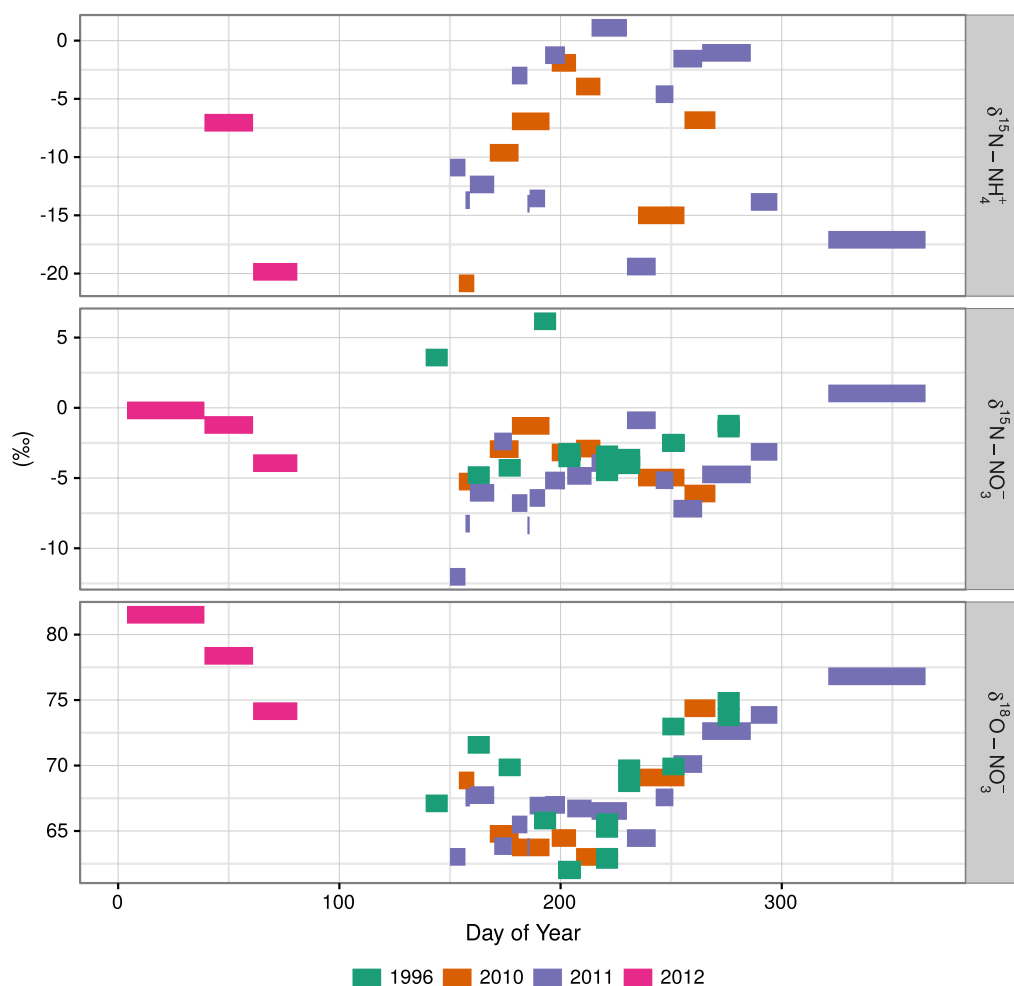


**Fig. 3.** Annual and open water season (OWS) dissolved inorganic nitrogen deposition ratios ( $\text{NH}_4^+/\text{NO}_3^-$ ) at the Experimental Lakes Area for the period from 1970 to 2013. Grey bands are the 95% confidence intervals around the linear regressions.



**Fig. 4.** Precipitation  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  values from the Experimental Lakes Area.



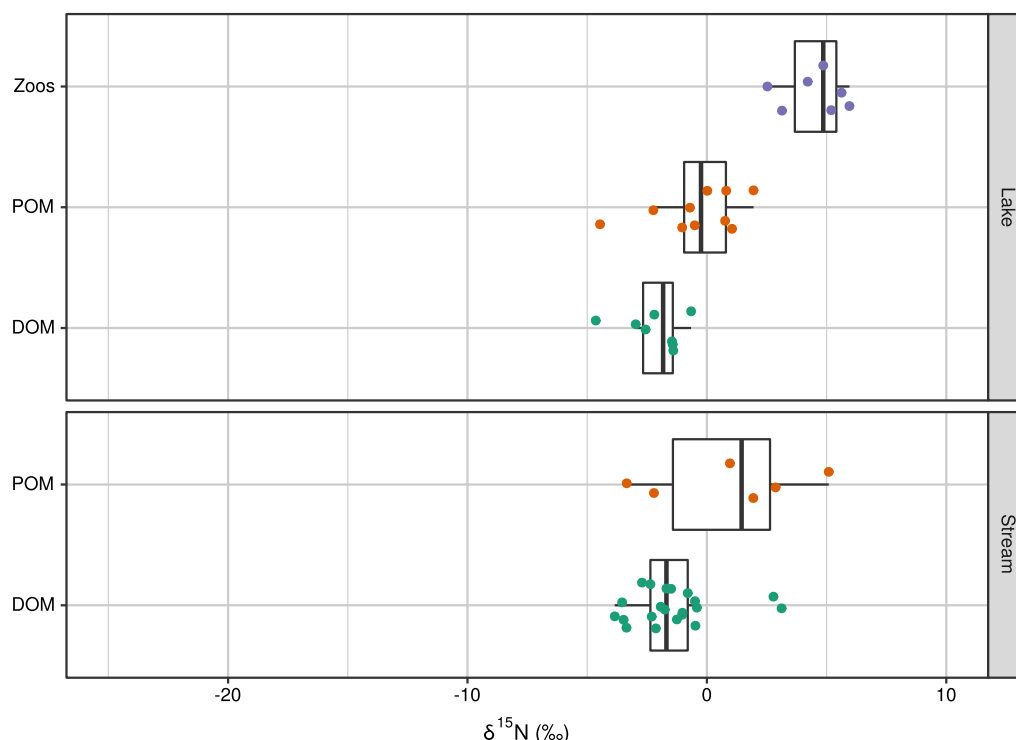


**Fig. 5.** Precipitation  $\delta^{15}\text{N-NH}_4^+$ ,  $\delta^{15}\text{N-NO}_3^-$ , and  $\delta^{18}\text{O-NO}_3^-$  values from the Experimental Lakes Area as function of the day of the year. Samples were collected between 17 July 1996 and 27 September 1996, and 3 June 2010 and 21 March 2012. Bar width represents the duration of bulk sample collection and height represents error associated with measurement.

$p = 0.23$ ). The mass-weighted mean of  $\delta^{15}\text{N-NH}_4^+$  deposition at the ELA ( $-7.4\text{‰}$ ) is close to the mean of published values at  $-6.4\text{‰}$ , but much lower than the mean value published for  $\delta^{15}\text{N-NO}_3^-$  ( $-2.7\text{‰}$ ). These are the first  $\delta^{15}\text{N-NH}_4^+$  values for Canadian precipitation and among the few for low-to-moderate  $\text{NH}_4^+$  deposition sites. The high intra-annual variability of  $\delta^{15}\text{N}$  in deposition implies that if a large precipitation event situated at one end of the isotopic range is missed, mass-weighted  $\delta^{15}\text{N}$  values may not be accurate. Given that the  $\delta^{15}\text{N-NH}_4^+$  values follow a trend similar to  $\delta^{15}\text{N-NO}_3^-$ , with the highest  $\delta^{15}\text{N}$  values in mid-summer, characterizing N inputs to watersheds and lakes will require a comprehensive year-round sampling regimen.

## N isotopes in lakes and streams

$\delta^{15}\text{N-NH}_4^+$  and  $\delta^{15}\text{N-NO}_3^-$  values in precipitation were lower and had a much wider range than  $\delta^{15}\text{N}$  in stream and lake DOM, POM, and zooplankton (Fig. 6). Additionally,  $\delta^{15}\text{N}$  deposition values exhibited much larger ranges than stream and lake values. Once filtered through the forest, wetlands,



**Fig. 6.**  $\delta^{15}\text{N}$  values of precipitation  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , lake and stream zooplankton (Zoos), particulate organic matter (POM), and dissolved organic matter (DOM) at the Experimental Lakes Area.

and soil of the catchment, the  $\delta^{15}\text{N}$ -TN values exported to lakes, largely as DOM (Parker et al. 2009), were about  $-3\text{‰}$  to  $-1\text{‰}$  (Fig. 6); very similar to the small amounts of  $\text{NO}_3^-$  released from forested catchments (Spoelstra et al. 2001; Mayer et al. 2002), but slightly higher than atmospheric deposition. This N has several in-lake fates, each of which incurs isotopic fractionation: cycling through the microbial loop, entering and transferring within the food web, deposition to sediments, nitrification, denitrification, and export via the outflow. Differences in  $\delta^{15}\text{N}$  values between direct atmospheric N deposition and N exported from forested catchment may help identify the relative importance of different sources of N to the ELA lakes. Additionally, these differences in  $\delta^{15}\text{N}$  values will be incorporated into food webs and may be recorded in lake sediments.

## Discussion

### Historical deposition

The 45 year record of N deposition at the ELA is unique in Canada and allows for analyses of changing climate and atmospheric deposition in a remote region of North America that previously had low dissolved inorganic N ( $\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$ ) deposition (Parker et al. 2009).

Large increases in  $\text{NH}_4^+$  deposition at the ELA lead to the observed increasing trend in the  $\text{NH}_4^+$  to  $\text{NO}_3^-$  ratio of atmospheric N deposition. Increasing  $\text{NH}_4^+$  in the bulk deposition collectors at the ELA is likely in the form of wet deposition. Dry deposition of  $\text{NH}_4^+$  typically occurs over short distances (1–2 km) from sources, whereas the atmospheric residence time for dissolved  $\text{NH}_4^+$  is approximately 10 d (Asman et al. 1998). This allows for the transport of dissolved  $\text{NH}_4^+$  for hundreds of kilometres. The observed increase in  $\text{NH}_4^+$  deposition at the ELA may be a result of

regional changes. Prevailing wind direction at the ELA is from the west where the plains and prairie landscapes in Manitoba, Saskatchewan, North Dakota, and parts of Minnesota are used for agriculture (e.g., Honey 2010).

Heavily farmed land leads to increased emissions of  $\text{NH}_3$  to the atmosphere through the application of  $\text{NH}_4^+$  fertilizer and N as manure (Asman et al. 1998). Both crop and animal farming result in  $\text{NH}_3$  volatilization (Lee et al. 2011). In Manitoba, fertilizer application increased four-fold from 1970 to 2011 (Fig. S5). In those four decades, the number of hogs increased by an order of magnitude and cattle have increased by 25% (Fig. S5) (Honey 2010).  $\text{NH}_4^+$  deposition has increased in the midwestern USA over the period from 1985 to 2012 (Du et al. 2014). However, unlike the ELA, the midwestern and northeastern USA show a decline in  $\text{NO}_3^-$  deposition that has partially to totally countered the increase in  $\text{NH}_4^+$  deposition, resulting in no trend in TN deposition at the national scale (Du et al. 2014).

The ELA deposition record shows a two-fold increase in  $\text{NH}_4^+$  over 40 years, whereas  $\text{NO}_3^-$  deposition has not changed. Atmospheric DIN ( $\text{NH}_4^+ + \text{NO}_3^-$ ) deposition during the 1990s was 4.6 kgN/(ha-year) and slightly higher than other forested boreal sites at that time: 3.7 kgN/(ha-year) at Lac Laflamme, Québec; 2.8 kgN/(ha-year) at Lac de la Tirasse, Québec (Watmough et al. 2005); and 2.3 kgN/(ha-year) at modeled boreal forests (Holland et al. 1999). These rates are all lower than 8.7 kgN/(ha-year) at TLW, east of Lake Superior (Spoelstra 2004). In the past 10 years, N deposition at the ELA has continued to rise (for 2013, the trend line indicates that DIN deposition is 5.4 kgN/(ha-year) and TN deposition is 6.7 kgN/(ha-year)), contemporaneously with the increase in agricultural intensity in Manitoba and the prairies. As a result, the ELA is no longer among the sites of lowest N deposition, with higher N deposition than the USA national mean (3.5 kgN/(ha-year)) (Du et al. 2014).

## Lakes: big and small

Separating the sources, processes, and fate of N in catchments, lakes, and food webs requires isotopic separation between the sources and adequate knowledge of the factors affecting isotopic fractionation (Bond and Diamond 2011; Parnell et al. 2013; Phillips et al. 2014). Terrestrially derived N is mainly in the form of DON, except for some  $\text{NO}_3^-$  exported during spring snowmelt that has undergone little in-stream or soil processing (Lamontagne and Schiff 1999; Burns and Kendall 2002). Forests retain almost all atmospherically deposited N in the growing season, with some small leakage as DON, especially during storms. At the ELA, direct N deposition to the lake surface accounts for one- to two-thirds of the annual N load to these small headwater lakes, depending on the catchment-to-lake-area ratio (Schindler et al. 1976; Flinn 2012). Given that the terrestrial stream flow is minimal in summer and snowmelt precedes ice-off, atmospheric N dominates the open water season N inputs to lakes. At the ELA, atmospheric  $\delta^{15}\text{N}$  of TN is lower than the terrestrial inputs and increasing deposition of  $\text{NH}_4^+$  that is especially low in  $\delta^{15}\text{N}$  compared with terrestrial inputs may provide some information for identifying N sources and processes.

The range in  $\delta^{15}\text{N}$ - $\text{NH}_4^+$  values is large (22%); twice as large as the total N isotopic enrichment expected by the maximum length of aquatic food webs at the ELA (e.g., 2.6‰ per trophic level; see Kidd et al. 1999; Vinebrooke et al. 2001). Because  $\text{NH}_4^+$  is rapidly assimilated in unproductive lakes,  $\text{NH}_4^+$  epilimnetic concentrations in summer are typically  $<10 \mu\text{gN/L}$ . In some non-impacted headwater lake systems, atmospheric N deposition can be 50% or more of total N input (Schindler et al. 1976; Findlay et al. 1994) and an even more important component of the summer N supply when terrestrial upland systems can become disconnected from downstream lakes. Changes in the  $\delta^{15}\text{N}$  value of the N supply with time will affect baseline values assigned to food webs. Further, the change in the ratio of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  may alter the food web structure given that the degree of preference for  $\text{NH}_4^+$  over  $\text{NO}_3^-$  is species specific (Dortch 1990; Fogel and Cifuentes 1993; Glibert et al. 2016).

In Lake Superior, where  $\text{NO}_3^-$  concentrations have been increasing over the last 50 years (Dove and Chapra 2015), atmospheric N deposition is a large input in the overall N budget, approximately equal in magnitude to terrestrial N loading (Sterner et al. 2007). The underlying mechanisms for this increase are unknown, spurring N cycling research in this large lake (e.g., Berges et al. 2014). Recent work using  $\text{NO}_3^-$  isotopes considered only atmospheric and river  $\text{NO}_3^-$  values due to the lack of  $\delta^{15}\text{N}-\text{NH}_4^+$  data. In those studies (Finlay et al. 2007; Sterner et al. 2007), the  $\delta^{15}\text{N}$  of inputs was higher than the observed  $\delta^{15}\text{N}-\text{NO}_3^-$  in the lake. Given that the ELA is immediately to the west of Lake Superior, that  $\text{NH}_4^+$  deposition is increasing, and  $\delta^{15}\text{N}-\text{NH}_4^+$  is quite low, the role of  $\text{NH}_4^+$  in the increasing  $\text{NO}_3^-$  concentrations and affecting the interpretation of N sources in Lake Superior using  $\delta^{15}\text{N}$  merits further attention (e.g., Kumar et al. 2008).

Finally, increasing  $\text{NH}_4^+$  in deposition coupled with its low  $\delta^{15}\text{N}-\text{NH}_4^+$  values has the potential to shift the  $\delta^{15}\text{N}$  of sediments in lakes by affecting either the terrestrial organic N input or food web baseline value. Increases in  $\text{NH}_4^+$  release as a result of agricultural activities (Galloway et al. 2003, 2004; Elser 2011) of low  $\delta^{15}\text{N}$  could provide one explanation for decreasing  $\delta^{15}\text{N}$  values in lake sediments that has been observed globally over the past 100 years (Holtgrieve et al. 2011).

Despite a lack of  $\delta^{15}\text{N}-\text{NH}_4^+$  data across Canada, the much lower  $\delta^{15}\text{N}-\text{NH}_4^+$  values in atmospheric deposition relative to  $\delta^{15}\text{N}-\text{NO}_3^-$  may aid in identifying overall changes in N cycling from large-scale changes in agricultural fertilizer and tilling practices, land-use changes such as oil sands development and forestry, and climate change.

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## Author contributions

Conceived and designed the study: JJV, SLS, MJP. Performed the experiments/collected the data: JJV, SLS, MJP, NAPF, HS, RJE. Analyzed and interpreted the data: JJV, SLS, MJP, NAPF, HS, RJE. Contributed resources: JJV, SLS, MJP, RJE. Drafted or revised the manuscript: JJV, SLS, MJP, NAPF.

## Competing interests

The authors have declared that no competing interests exist.

## Data accessibility statement

All relevant data are within the paper, the Supplementary Material, and archived at doi:10.5281/zenodo.276297.

## Supplementary material

The following Supplementary Material is available with the article through the journal website at doi:10.1139/facets-2016-0060.

Supplementary Material 1

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