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Key Points:

- Lake sediments can record trends in the atmospheric deposition of reactive nitrogen (Nr)
- Watershed N retention affects whether lake sediment $\delta^{15}\text{N}$ is related to Nr deposition
- The interactive effects of climate and nutrients force changes in algal communities

Supporting Information:

- Supporting Information S1

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Nitrogen deposition to lakes in national parks of the western Great Lakes region: Isotopic signatures, watershed retention, and algal shifts

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Abstract Atmospheric deposition is a primary source of reactive nitrogen (Nr) to undisturbed watersheds of the Great Lakes region of the U.S., raising concerns over whether enhanced delivery over recent decades has affected lake ecosystems. The National Atmospheric Deposition Program (NADP) has been measuring Nr deposition in this region for over 35 years. Here we explore the relationships among NADP-measured Nr deposition, nitrogen stable isotopes ($\delta^{15}\text{N}$) in lake sediments, and the response of algal communities in 28 lakes situated in national parks of the western Great Lakes region of the U.S. We find that 36% of the lakes preserve a sediment $\delta^{15}\text{N}$ record that is statistically correlated with some form of Nr deposition (total dissolved inorganic N, nitrate, or ammonium). Furthermore, measured long-term (since 1982) nitrogen biogeochemistry and inferred critical nitrogen loads suggest that watershed nitrogen retention and climate strongly affect whether sediment $\delta^{15}\text{N}$ is related to Nr deposition in lake sediment records. Measurements of algal change over the last ~150 years suggest that Nr deposition, in-lake nutrient cycling, and watershed inputs are important factors affecting diatom community composition, in addition to direct climatic effects on lake physical limnology. The findings suggest that bulk sediment $\delta^{15}\text{N}$ does reflect Nr deposition in some instances. In addition, this study highlights the interactive effects of Nr deposition and climate variability.

1. Introduction

The atmospheric deposition of nitrogen (N) is a primary source of fixed N to aquatic ecosystems in the Great Lakes region of the U.S. Lake Superior not only gets an estimated 70% of its incoming nitrate (NO_3) from the atmosphere and about 27% of all N from direct deposition but also produces a significant amount internally through nitrification [Finlay et al., 2007; Sterner et al., 2007]. The global doubling of N in the environment as a result of human activities has led to significant loading of reactive N (Nr) to historically N limited aquatic ecosystems [Elser et al., 2009]. Boreal lakes in North America and Europe, which were historically N limited, have experienced sufficient Nr deposition to increase algal productivity in some cases [Axler et al., 1994; Bergström and Jansson, 2006]. Nr deposition and algal N requirements have also been strongly linked to changes in algal communities in alpine lakes [Lafrancois et al., 2003; Wolfe et al., 2003; Saros et al., 2005; Hobbs et al., 2010].

Nitrogen inputs to the Great Lakes region and climate warming have been suggested as two dominant stressors on aquatic ecosystems [McDonald et al., 2010]. The idea that ecosystems have a threshold for stressors, such as Nr deposition, has been quantified in various studies as a critical load [Baron, 2006; Pardo et al., 2011; Saros et al., 2011]. In lakes of the western Great Lakes region of the U.S., the main impact of Nr deposition is likely to be increased productivity [Axler et al., 1994; Daggett et al., 2015], as the acid-neutralizing capacity of the soils and surface waters suggests there is low or no sensitivity to acidification [Stottlemeyer et al., 1998; Kallemeyn et al., 2003]. When considering the impacts to lakes from Nr deposition and climate warming, the reality is likely an interactive stress [Hobbs et al., 2010; Baron et al., 2013].

Nr saturation of a watershed occurs when atmospheric N inputs exceed the capacity of the ecosystem to assimilate it [Aber et al., 1989; Stoddard, 1994]. Nr saturation has generally impacted forests of the Upper Midwest U.S. to a lesser degree than intact forests of Europe or the northeast U.S. [Dise and Wright, 1995; Driscoll et al., 2003]. There are four stages of watershed N loss due to saturation proposed

by Aber *et al.* [1989] and described empirically by Stoddard [1994]: (0) little or no NO_3 leakage from the watershed during the growing season, with small amounts of NO_3 in the snowmelt runoff; (1) minimal NO_3 leakage during the growing season but high concentrations of NO_3 in runoff pulses and spring N limitation is delayed in lakes; (2) watershed NO_3 uptake is less efficient with a loss of NO_3 during the winter and spring and to the groundwater during the growing season; (3) no N sinks in the watershed and all inputs, including mineralized N, are lost. Generally, lakes in the early stages (0 and 1) of watershed N loss tend to be in regions of low Nr deposition, while lakes in the later stages (2 and 3) are often in regions of high atmospheric deposition [Stoddard, 1994].

The measured deposition of dissolved inorganic nitrogen (DIN) in precipitation has been shown to correlate well with Nr loading in high-elevation lakes [Williams *et al.*, 1996; Mast *et al.*, 2014] and lakes in forested watersheds [Canham *et al.*, 2012]. A number of studies have demonstrated the utility of stable isotopes of nitrate-N ($\delta^{15}\text{N}\text{-NO}_3$) as a tool for assessing the source contributions of NO_x to a site [Elliott *et al.*, 2007; Nanus *et al.*, 2008]. Lake sediment $\delta^{15}\text{N}$ records have been used as a proxy to broadly infer the extent of changes in atmospheric Nr over time [Holtgrieve *et al.*, 2011; Wolfe *et al.*, 2013] and to infer ecological changes induced by Nr deposition [Wolfe *et al.*, 2003]. Less clear is whether or not sediment $\delta^{15}\text{N}$ directly reflects the measured DIN load from the atmosphere.

In this study we address two main questions: (1) Do sediment $\delta^{15}\text{N}$ records faithfully record measured Nr deposition (kg ha^{-1}) across a range of northern lakes, and (2) are recent changes in lake algal (mainly diatom) communities related to the deposition of Nr? Here we show that measured Nr deposition correlates with lake sediment $\delta^{15}\text{N}$ in a number of lakes and that those lakes are located in watersheds which are suspected of having high N retention where shallow subsurface flow during snowmelt is the main pathway for NO_3 transport. Furthermore, in the majority of lakes, diatom community change is correlated with sediment $\delta^{15}\text{N}$, which we suggest reflects inputs of nutrients—both directly through atmospheric deposition and indirectly through watershed contributions—and climate variability.

2. Materials and Methods

2.1. Study Sites

This study focuses on 28 lakes situated in the vicinity of Lake Superior and Lake Michigan in the western Great Lakes region of the United States (Figure 1). Twenty-four are located in national parks, while three others are located along the north shore highlands of Lake Superior. The study units include: Voyageurs National Park, near Grand Portage National Monument, Isle Royale National Park, Apostle Islands National Lakeshore, St. Croix National Scenic Riverway, Pictured Rocks National Lakeshore, and Sleeping Bear Dunes National Lakeshore (Table 1). The lakes cover large gradients in physical and chemical characteristics (Table 1). Most watersheds are within the Northern Forests ecoregion [Commission for Environmental Cooperation, 1997] and generally dominated by spruce (*Picea* spp.), fir (*Abies* spp.), aspen (*Populus* spp.), and birch (*Betula* spp.). Sleeping Bear and St. Croix are situated in the North Central Hardwood Forests ecoregion, dominated by northern hardwoods of maple (*Acer* spp.), beech (*Fagus grandifolia*), and birch (*Betula* spp.). The climate of the region is cold continental—warm in the summer and very cold in the winter—with the majority of annual precipitation falling as snow. The dominant air masses that control the weather are generally from the north for most of year and the south in the spring to summer. The wind shifts from northwest-southwest to south-southwest in late winter (March) associated with an increase in low-pressure systems across the Upper Great Lakes [Stottlemeyer *et al.*, 1998]. This increases atmospheric concentrations of Nr from urban sources in late winter.

Most of the parks have been directly impacted by human activity or stochastic events in the past that could impact the long-term sediment records of $\delta^{15}\text{N}$ and algal community turnover. Almost all the parks were settled in the late 1800s by Euro-Americans who altered the landscape by logging, land clearance, and dam construction [Edlund *et al.*, 2011]. At Sleeping Bear there was a period of land clearance and small-scale farming from 1900 to 1950; the park was established in 1970. At Voyageurs (established 1975), logging began in the late 1800s and continued into the early 1900s, small-scale mining at Rainy lake took place in the late 1800s and dam construction in the early 1900s has continued to regulate water levels in the parks' largest lakes. Apostle Islands was established in 1970; the islands were settled in the late 1800s and farming, logging,

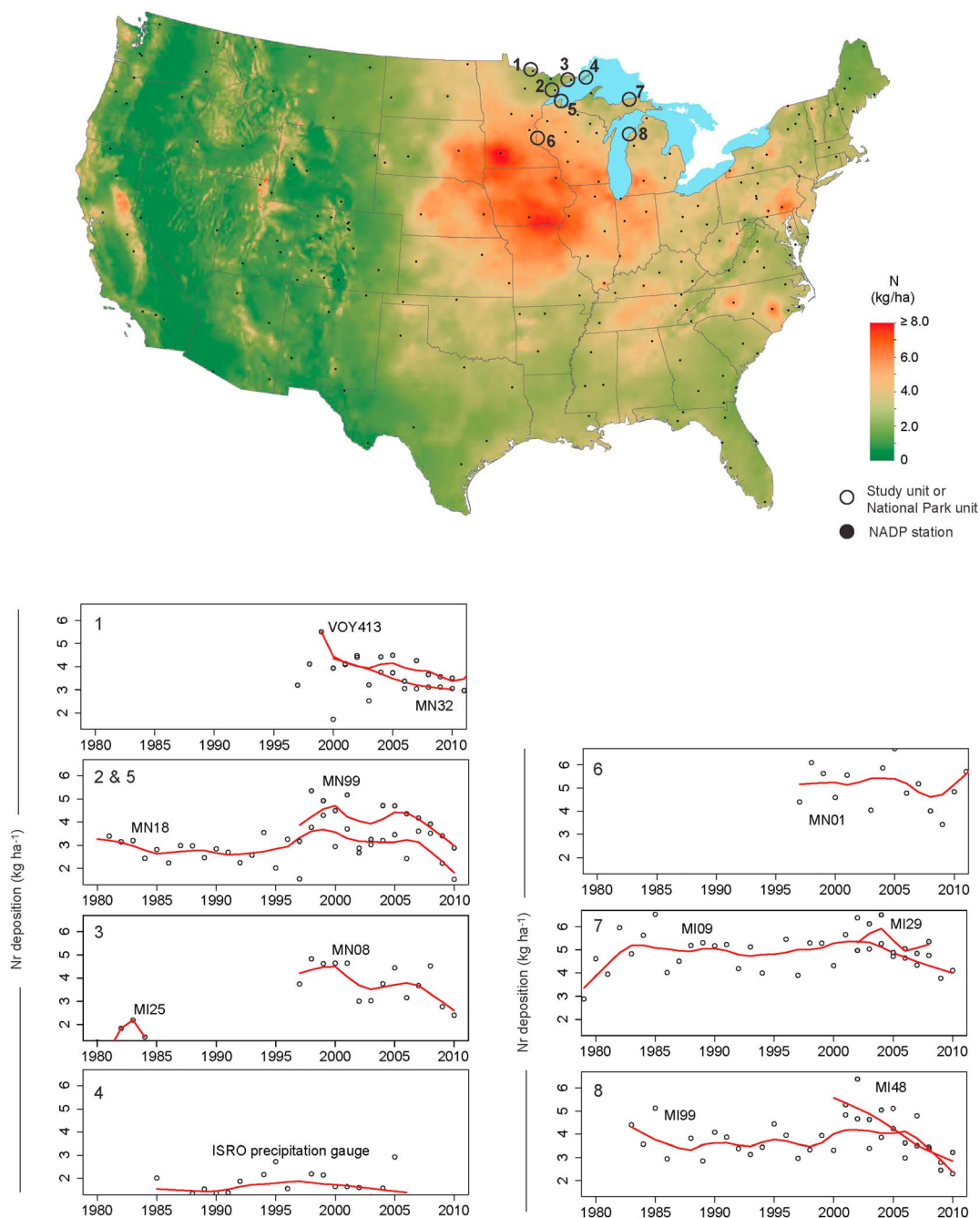


Figure 1. Map of NADP Nr deposition data for 2010 [NADP, NRSP-3, 2010]. Study units are (1) Voyageurs National Park, (2) greater Minnesota, (3) near Grand Portage National Monument, (4) Isle Royale National Park, (5) Apostle Islands National Lakeshore, (6) St. Croix National Scenic Riverway, (7) Pictured Rocks National Lakeshore, and (8) Sleeping Bear Dunes National Lakeshore. Nr deposition trends used for each of the study units are below the map with loess smooth curve fit to each. Unit for Nr deposition is kg ha^{-1} of DIN expressed as molecular weight ($\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$).

stone quarrying, and commercial fishing took place until the 1950s. Pictured Rocks was designated as National Lakeshore in 1966; the area was logged in the late 1800s until 1910. St. Croix was one of the original scenic rivers under the National Wild and Scenic Rivers Act of 1968. At Isle Royale, small-scale copper mining took place sporadically in the late 1800s to early 1900s, logging took place in the early 1900s, and large fires burned in 1936 [Scarpino, 2011]. Isle Royale was designated a wilderness area in 1976. The Wallace Lake watershed at Isle Royale has been the site of long-term biogeochemical monitoring since 1982 [Stottlemeyer *et al.*, 1998].

Table 1. Physical and Chemical Attributes of the Study Sites^a

Lake	Latitude	Longitude	Year Core Taken	Park	NADP Site	NADP Start Date	Maximum Depth (m)	Lake Area (ha)	Watershed Area (ha)	WA:LA N ($\mu\text{g L}^{-1}$)	Dissolved Inorganic Phosphorus ($\mu\text{g L}^{-1}$)	Total Phosphorus ($\mu\text{g L}^{-1}$)	DIN:TP (Mass)	Reference
Outer Lagoon	47.004173	-90.4597519	2007	APIS	WI36,MN99	1980	1.4	22.0	70	3.2	1.7	10.0	0.2	Edlund et al. [2011] and this study
Tetagouche Lake	47.3449135	-91.2686615	1996, 2009	greater MN	MN99,MN18	1980	4.6	27.0	103	3.8	50.0	17.0	2.9	Engstrom et al. [2007]
August	47.762531	-91.608573	1996, 2009	greater MN	MN18	1980	5.8	90.0	unk ^c		50.0	14.0	3.6	Engstrom et al. [2007]
Nipisiquit	47.355569	-91.247845	1996, 2009	greater MN	MN99,MN18	1980	5.5	24.0	298.0	12.4	unk	16.0	unk	Engstrom et al. [2007]
Harvey Lake	48.05067	-88.79602	2007	ISRO	MI97 ^b ,MI25	1980	4.0	55.4	341.0	6.2	3.0	14.0	0.2	Edlund et al. [2011] and this study
Richie Lake	48.04092	-88.70236	2007	ISRO	MI97 ^b ,MI25	1980	10.7	216.2	1186.2	5.5	4.0	33.7	0.1	Edlund et al. [2011] and this study
Wallace Lake	48.057148	-88.627924	2011	ISRO	MI97 ^b ,MI25	1980	3.0	4.0	115.0	28.8	unk	unk	unk	Stottlemeyer et al. [1998]
Desor Lake	47.976328	-88.985065	2010	ISRO	MI97 ^b ,MI25	1980	14.0	427.8	1436.7	3.4	2.5	11.3	0.2	Edlund et al. [2011] and this study
Intermediate Lake	48.0304239	-88.7283577	2006	ISRO	MI97 ^b ,MI25	1980	6.7	71.0	481.7	6.8	5.0	14.0	0.4	Edlund et al. [2014], Drevnick et al. [2007], Kraft et al. [2010], and Kallemeyn [2000]
Ahmik Lake	48.14787	-88.54153	2007	ISRO	MI97 ^b ,MI25	1980	3.4	10.3	358.7	34.8	3.3	14.7	0.2	Edlund et al. [2011] and this study
Lake Superior, Moskey Inlet	48.068972	-88.5663986	2007	ISRO	MI97 ^b ,MI25	1980	14.7	unk	unk	unk	unk	unk	unk	Edlund et al. [2011] and this study
Siskiwit Lake	48.0005271	-88.7956283	2010	ISRO	MI97 ^b ,MI25	1980	46.0	1635.0	7239.4	4.4	15.4	3.4	4.5	Edlund et al. [2014] and this study
Swamp Lake	47.951333	-89.858083	2006	nr GRPO	MN08,MI25	1980	5.8	143.7	1458.4	10.1	141.7	30.7	4.6	Lafrancois et al. [2009b], Edlund et al. [2007], and this study
Speckled Trout Lake	47.95	-89.8463	2006	nr GRPO	MN08,MI25	1980	6.4	25.9	113.7	4.4	48.3	23.5	2.1	Lafrancois et al. [2009b], Edlund et al. [2007], and this study
Grand Sable	46.641305	-86.0357166	2005	PIRO	MI48,MI99	1983	26.0	255.0	4143.5	16.2	8.7	6.3	1.4	Damstra et al. [2014] and Mechenich et al. [2006]
Beaver Lake	46.56524	-86.34362	2008	PIRO	MI48,MI99	1983	10.0	310.0	3030.0	9.8	6.3	10.0	0.6	Edlund et al. [2011], Damstra et al. [2014], and Mechenich et al. [2006]
Lake St. Croix 6B	44.947549	-92.7553722	2010	SACN	MN01	1996	14.9	3530.0	1999500.0	566.4	606.3	55.6	10.9	Edlund et al. [2009], Lafrancois et al. [2009a], and this study
Bass Lake	44.9231008	-85.884445	2005	SLBE	MI29,MI09	1979	7.0	38.0	unk	unk	27.0	10.3	2.6	Edlund et al. [2011] and Damstra et al. [2014]
Lake Manitou	45.12693	-86.0237	2005	SLBE	MI29,MI09	1979	14.0	104.0	914.0	8.8	10.7	19.0	0.6	Edlund et al. [2011] and Damstra et al. [2014]
Florence Lake	45.010527	-86.1198853	2005	SLBE	MI29,MI09	1979	8.0	32.0	557.5	17.4	51.0	19.3	2.6	Edlund et al. [2011] and Damstra et al. [2014]
Cruiser Lake	48.49753	-92.80225	2006	VOYA	MN32/VOY413	1996	27.7	46.5	162.8	3.5	3.7	3.7	1.0	Edlund et al. [2011] and this study
Ek Lake	48.46975	-92.836	2006	VOYA	MN32/VOY413	1996	5.8	36.0	255.6	7.1	8.0	16.3	0.5	Edlund et al. [2011] and this study
Peary Lake	48.52423	-92.77164	2006	VOYA	MN32/VOY413	1996	4.6	45.3	976.4	21.6	12.3	18.0	0.7	Edlund et al. [2011] and this study
Namakan Lake	48.4338	-92.702267	2005	VOYA	MN32/VOY413	1996	45.7	10170.0	1959759.0	192.7	57.0	12.6	4.5	Edlund et al. [2011] and this study

Table 1. (continued)

Lake	Latitude	Longitude	Year Core Taken	Park	NADP Site	NADP Start Date	Maximum Depth (m)	Lake Area (ha)	Watershed Area (ha)	WA:LA N ($\mu\text{g L}^{-1}$)	Dissolved Inorganic Phosphorus ($\mu\text{g L}^{-1}$)	Total Phosphorus DIN:TP (Mass)	Reference	
Kabetogama Lake	48.4557667	-92.95295	2005	VOYA	MN32/VOY413	1996	24.3	10425.0	2050597.5	196.7	10.0	35.4	0.3	Edlund <i>et al.</i> [2011], this study, Christensen <i>et al.</i> [2004], and Kallemeyn <i>et al.</i> [2003]
Rainy Lake	48.539183	-92.8291833	2005	VOYA	MN32/VOY413	1996	49.1	92100.0	3858990.0	41.9	66.0	14.0	4.7	Edlund <i>et al.</i> [2011], this study, Christensen <i>et al.</i> [2004], Kallemeyn <i>et al.</i> [2003]
Little Trout	48.396615	-92.522264	2010	VOYA	MN32/VOY413	1996	29.0	96.7	251.4	2.6	8.8	4.8	1.8	Edlund <i>et al.</i> [2008], this study, Christensen <i>et al.</i> [2004], and Kallemeyn <i>et al.</i> [2003]
Mukooda Lake	48.334024	-92.488719	2010	VOYA	MN32/VOY413	1996	23.8	305.0	762.5	2.5	50.0	8.3	6.0	Edlund <i>et al.</i> [2011], <i>Mechenich et al.</i> [2010], and this study
^a VOYA = Voyageurs National Park; nr GRPO = near Grand Portage National Monument; ISRO = Isle Royale National Park; APIS = Apostle Islands National Lakeshore; SACN = St. Croix National Scenic Riverway; PIRO = Pictured Rocks National Lakeshore; SLBE = Sleeping Bear Dunes National Lakeshore. ^b M197 was OPERATED for 2 years, after which time a continuous bulk precipitation collector was operated by Michigan Technological University. cunk = unknown.														

^aVOYA = Voyageurs National Park; nr GRPO = near Grand Portage National Monument; ISRO = Isle Royale National Park; APIS = Apostle Islands National Lakeshore; SACN = St. Croix National Scenic Riverway; PIRO = Pictured Rocks National Lakeshore; SLBE = Sleeping Bear Dunes National Lakeshore.

^bM197 was OPERATED for 2 years, after which time a continuous bulk precipitation collector was operated by Michigan Technological University.

^cunk = unknown.

Field methods for the Wallace Lake long-term site are described in Stottlemeyer [1997] and Stottlemeyer *et al.* [1998]. Methods and variables addressed in this study (NO_3 , NH_4 , flow, wet deposition chemistry, and snow-pack) have remained consistent throughout the period of monitoring.

2.2. Sediment Coring and Dating

All lakes, with the exception of Wallace Lake, were cored as part of previous studies (Table 1). The same methods were used for each lake; a sediment core was recovered from canoe or boat using a piston-type corer [Wright, 1991]. Cores were subsampled at a resolution of 0.5–1.0 cm, freeze-dried and prepared for diatom and geochemical analysis. Geochronology was established through ^{210}Pb decay (measured as ^{210}Po) by alpha spectrometry at the St. Croix Watershed Research Station [Eakins and Morrison, 1978]. The constant rate of supply (CRS) model was used to estimate sediment age and dry mass accumulation rate (DMAR) based on the distribution of excess (i.e., unsupported) ^{210}Pb above the depth at which background (or supported) and excess ^{210}Pb activity are in equilibrium [Appleby and Oldfield, 1978; Appleby, 2001]. All sediments were archived at the St. Croix Watershed Research Station until further analysis of nitrogen stable isotopes for this study.

2.3. Nitrogen Stable Isotopes

A total of 510 sediment core samples were analyzed for total N concentration and stable isotopic ratio ($\delta^{15}\text{N}$). Analysis was conducted by the University of California-Davis, Stable Isotope Facility, using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Quality control measures included the analysis of triplicate samples, where the coefficient of variation (CV) for %N was <5% (median of 1%) and the standard deviation for $\delta^{15}\text{N}$ was < 0.2‰ (median of 0.08‰). In addition, a project standard consisting of the same sediment core interval was analyzed with each run of $\delta^{15}\text{N}$ and had a CV of 2.5% N and a standard deviation of 0.12‰ $\delta^{15}\text{N}$ across all the runs.

2.4. Subfossil Diatom Remains

Samples for diatom analysis were prepared and enumerated using the protocols of

Battarbee *et al.* [2001] as detailed in National Parks Service (NPS) publications and reports [Ramstack *et al.*, 2008; Edlund *et al.*, 2011]. A minimum of 400 diatom valves were counted in each sample with identification based on regional taxonomic floras and monographs such as Patrick and Reimer [1966, 1975], Camburn *et al.* [1978, 1984–1986], Krammer and Lange-Bertalot [1986–1991], Cumming *et al.* [1995], Reavie and Smol [1998], Camburn and Charles [2000], Fallu *et al.* [2000], and the primary literature [e.g., Koppen, 1975]. For major taxa, digital images were taken and maintained in a database to achieve consistent taxonomy. All diatom counts were converted to percent abundances by taxon relative to total diatom counts in each sample.

2.5. Numerical Analysis

National Atmospheric Deposition Program (NADP) data were downloaded for each of the locations in the vicinity of the study sites [National Atmospheric Deposition Program (NADP), NRSP-3, 2010] (Table 1). The NADP site nearest to each lake was used for regression analysis. In order to directly compare the NADP deposition data to sediment records, the measured DIN loads (total, NO_3 , and NH_4) were averaged over an interval of time corresponding to the number of years represented by each sediment interval for each core. Simple linear regression was used to test whether sediment $\delta^{15}\text{N}$ and measured deposition chemistry (DIN, NH_4 , and NO_3) were correlated for each lake. Pearson's product-moment correlation values and p values were used to determine the significance of the correlations. This approach is similar to that in other studies comparing instrumental and paleolimnological data [Battarbee *et al.*, 2002]. Detrended correspondence analysis (DCA) was used to summarize the dominant gradient (i.e., DCA axis 1) of diatom compositional turnover [Hill and Gauch, 1980]. All diatom species were included in the analysis, detrending was by segments with down weighting of rare taxa, and nonlinear rescaling was applied. When summarized stratigraphically, the DCA axis 1 scores show the amount of turnover between samples over time in units of standard deviation (SD). A test for significance of DCA axis 1 was carried out by comparing with a random model (broken-stick model) [Jackson, 1993]. We also tested the diatom records for significant zonations using a hierarchical cluster analysis constrained to time with a Bray-Curtis dissimilarity metric. The zonations were also compared to broken-stick model to infer significance. All numerical analyses were carried out using R [R Core Team, 2013].

2.6. Lake Thermal Properties

In order to test the possible role climatic effects may have on structuring diatom communities by influencing lake thermal properties, we modeled the duration of stratification and number of ice-free days for four of our study lakes [Edlund *et al.*, 2014]. Detailed model validation can be found in Edlund *et al.* [2014]. Briefly, the model MINLAKE was used to predict the variables of interest from measured weather data (air temperature, wind speed, solar radiation, dew point temperature, precipitation, and sunshine percentage). MINLAKE uses weather data and lake physical parameters to describe the heat transfer with depth in the lake and is calibrated against measured water temperature data [Fang *et al.*, 2010]. Weather data dating back to 1962 from International Falls, MN, and Duluth, MN, were used in the model. With historical weather data sets the model predicts historical lake thermal properties. We are therefore able to compile a data set of various lake thermal properties, summarized at an annual resolution, to directly compare to our diatom DCA axis 1 scores.

3. Results

3.1. Sediment Dating

Each of the sediment cores was readily dated using ^{210}Pb . Near-surface ^{210}Pb activities were high ($10\text{--}123\text{ pCi g}^{-1}$; median of 28 pCi g^{-1}) indicating low rates of sediment accumulation, and downcore profiles were monotonic to near-exponential indicating relatively constant DMAR as would be expected for remote and minimally disturbed wilderness lakes (Figure S1 in the supporting information). The resulting age-depth models had a low degree of uncertainty in the upper section of the cores that would overlap with the NADP data records (i.e., post-1980). With the goal of this study to compare measured data to sediment core records, good age control for the period of interest (1980–2010) is imperative. The calculated error (standard deviation) from the CRS age models for each lake over this time period is ± 1 year ($n = 136$; mean of 1.1 years; 25th percentile of 0.73 years; 75th percentile of 1.4 years; Figure 2).

3.2. Sediment Diagenesis

Postdepositional diagenetic alterations of sediment $\delta^{15}\text{N}$ are a potential concern in the interpretation of sediment records [Teranes and Bernasconi, 2000; Gálman *et al.*, 2009; Holtgrieve *et al.*, 2011; Brahney *et al.*, 2014].

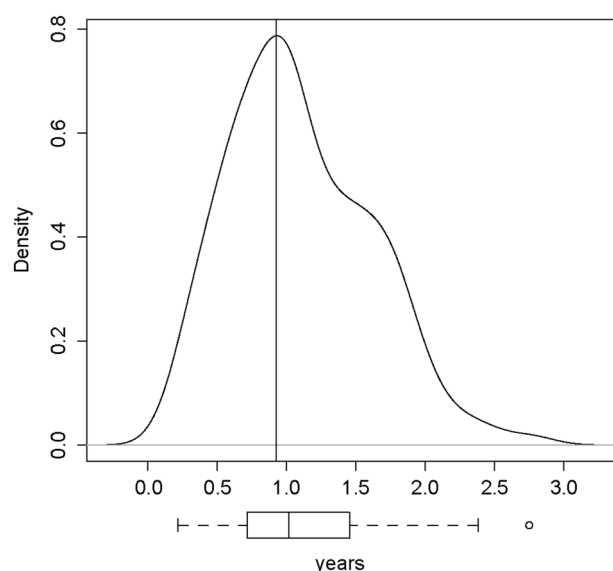


Figure 2. Density plot of the CRS ^{210}Pb age model error over the period of the NADP data. Vertical line is the peak of the density curve at 0.93. Boxplot beneath the density curve is the median with 25th and 75th percentile box.

Diagenetic changes reported in the literature indicate that no uniform pattern (depletion or enrichment) of sediment $\delta^{15}\text{N}$ is prevalent [Gälman *et al.*, 2009]. However, in cases where microbial alteration of the sediment is suspected, there has been a slight depletion in $\delta^{15}\text{N}$ (0.3–0.7‰) which is counterintuitive to kinetic fractionation, which suggests a preferential loss of ^{14}N and an enrichment of the sediment $\delta^{15}\text{N}$. In many cases the possible diagenetic depletion is much smaller than the range in $\delta^{15}\text{N}$ observed in the sediment core. Therefore, bulk sediment $\delta^{15}\text{N}$ should be viewed as a conservative estimate of the $\delta^{15}\text{N}$ of algal or aquatic biomass. Studies demonstrating that bulk sediment $\delta^{15}\text{N}$ is a conservative estimate have been undertaken using models [Brahney *et al.*, 2014] and by isolating the algal photosynthate [Enders *et al.*, 2008].

To explicitly address this issue, we analyzed three lakes from our data set with sediment

cores taken ~10 years apart and from the same location within each lake (Figure 3). Core sites were relocated through GPS, and the resulting ^{210}Pb profiles of the core pairs closely overlapped, confirming the core site match (Figure 3). The nitrogen isotope records for all three lakes demonstrate that the primary trend over time was preserved in sediment layers of the same age (all data, $r = 0.9$; $p < 0.001$), but with some deviations suggesting a diagenetic effect in the older core pair. In Nipisiquit, a near-surface spike in $\delta^{15}\text{N}$ was not preserved in the newer core, indicating preferential loss of the lighter isotope over time. However, the two profiles rapidly converge below this depth, indicating a relatively short period of postburial alteration of the $\delta^{15}\text{N}$ record (Figure 3). In the other two lakes there is an offset of 0.2–0.3‰ between the two records. In August Lake the newer core is more depleted, while in Tettegouche the newer core is more enriched. The cause of these deviations is unclear but may represent fine-scale spatial variability within lakes, or in the case of Tettegouche, the enrichment of older sediments due to microbial fractionation [Gälman *et al.*, 2009]. The important observation is that the primary trend of sediment $\delta^{15}\text{N}$ with depth remains stable.

3.3. Lake Sediment Nitrogen Isotopes

The absolute $\delta^{15}\text{N}$ values for the sediment cores ranged from -2.51 to 5.27 ‰. We analyze the sediment $\delta^{15}\text{N}$ trends as z scores, where $z = (\text{mean} - x)/\text{standard deviation}$, which standardizes the trends among all the records and allows for direct comparison. The temporal trend in sediment $\delta^{15}\text{N}$ is variable among lakes, although within individual parks there are some consistent patterns (Figure 4). For example, each of the sediment cores from VOYA have a background (pre-1900) value of ~ 3 ‰, while lakes in ISRO have background values that are more variable and depleted (Figure 4).

The trends in $\delta^{15}\text{N}$ from Voyageurs lakes are quite stable (range 0.15–4.96‰; variance 1.0); a couple of the lakes, Mukooda and Ek, exhibit a depletion in $\delta^{15}\text{N}$ beginning around 1950 (Figure 4). The Isle Royale lakes have $\delta^{15}\text{N}$ trends that are more variable (range -0.94 –2.93‰; variance 1.3); Ahmik, Intermediate, and Richie Lake exhibit a depletion in $\delta^{15}\text{N}$ that begins circa 1970, while Desor Lake shows a depletion at around 1950. Outer Lagoon in Apostle Islands has very low variance (range -2.23 to -0.14 ‰; variance 0.4) and also shows a depletion beginning around 1950. The lakes near Grand Portage, Speckled Trout and Swamp, have slowly declining trends in $\delta^{15}\text{N}$ which begin in the late 1800s for Swamp Lake and around 1940 for Speckled Trout Lake (range -2.51 –0.27‰; variance 0.67). Unlike any of the other lakes, Grand Sable and Beaver Lake on Pictured Rocks show an increasing trend, in particular an enrichment that begins circa 1970. Lake St. Croix has the most enriched $\delta^{15}\text{N}$ values and little variability in the trend (range 3.94–5.27‰; variance 0.18). The lakes on Sleeping Bear (Bass, Florence, and Manitou) show the most

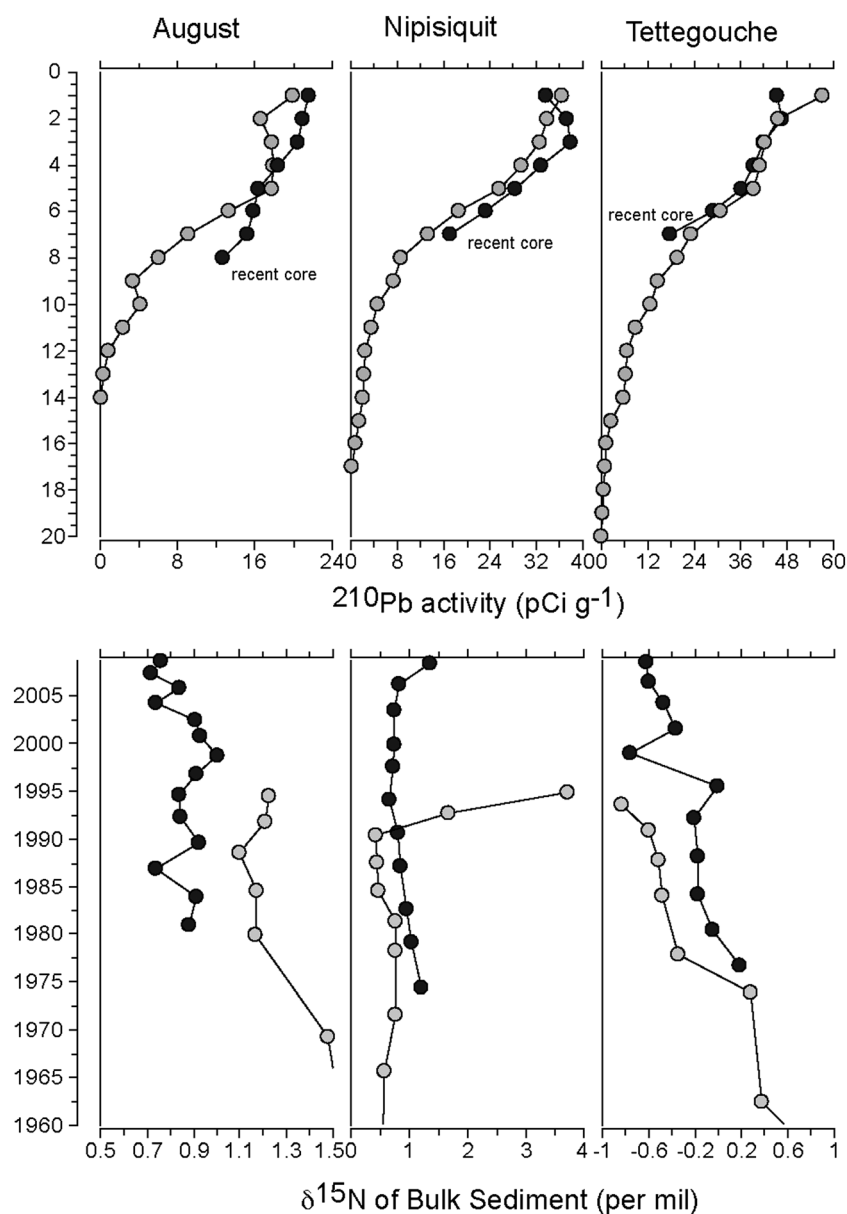


Figure 3. Lakes with duplicate cores retrieved approximately 10 years apart (black circles = recent core). (top) The ^{210}Pb activity with depth. (bottom) Bulk sediment $\delta^{15}\text{N}$ with depth.

variability in $\delta^{15}\text{N}$ trends (range -1.11 – 3.99‰ ; variance 2.15) and all three lakes show a depletion in the trend beginning around 1980 (postpark establishment) with greater change occurring in the early 1990s during a period of small-scale farming.

3.4. NADP Data

The National Atmospheric Deposition Program has records that extend back to 1980 at some sites. Of interest to our study are the records of nitrate (NO_3), ammonium (NH_4), and dissolved inorganic nitrogen (DIN) load (kg ha^{-1}). NADP maps detail the spatial gradient of Nr deposition across our study region [NADP, NRSP-3, 2010] (Figure 1). Generally, sites in the southern and eastern portions receive significantly higher loads of atmospheric Nr than sites near Lake Superior. The Nr deposition is variable across our study region (Figure 1). The station on Isle Royale has the lowest deposition ($\sim 1.5 \text{ kg ha}^{-1}$), while the Douglas Lake station on the Upper Peninsula of Michigan (MI09) has the highest deposition ($\sim 5 \text{ kg ha}^{-1}$), followed by the Chassell station (MI99) near Houghton, Michigan, on Lake Superior ($\sim 4 \text{ kg ha}^{-1}$) and Voyageurs ($\sim 4 \text{ kg ha}^{-1}$).

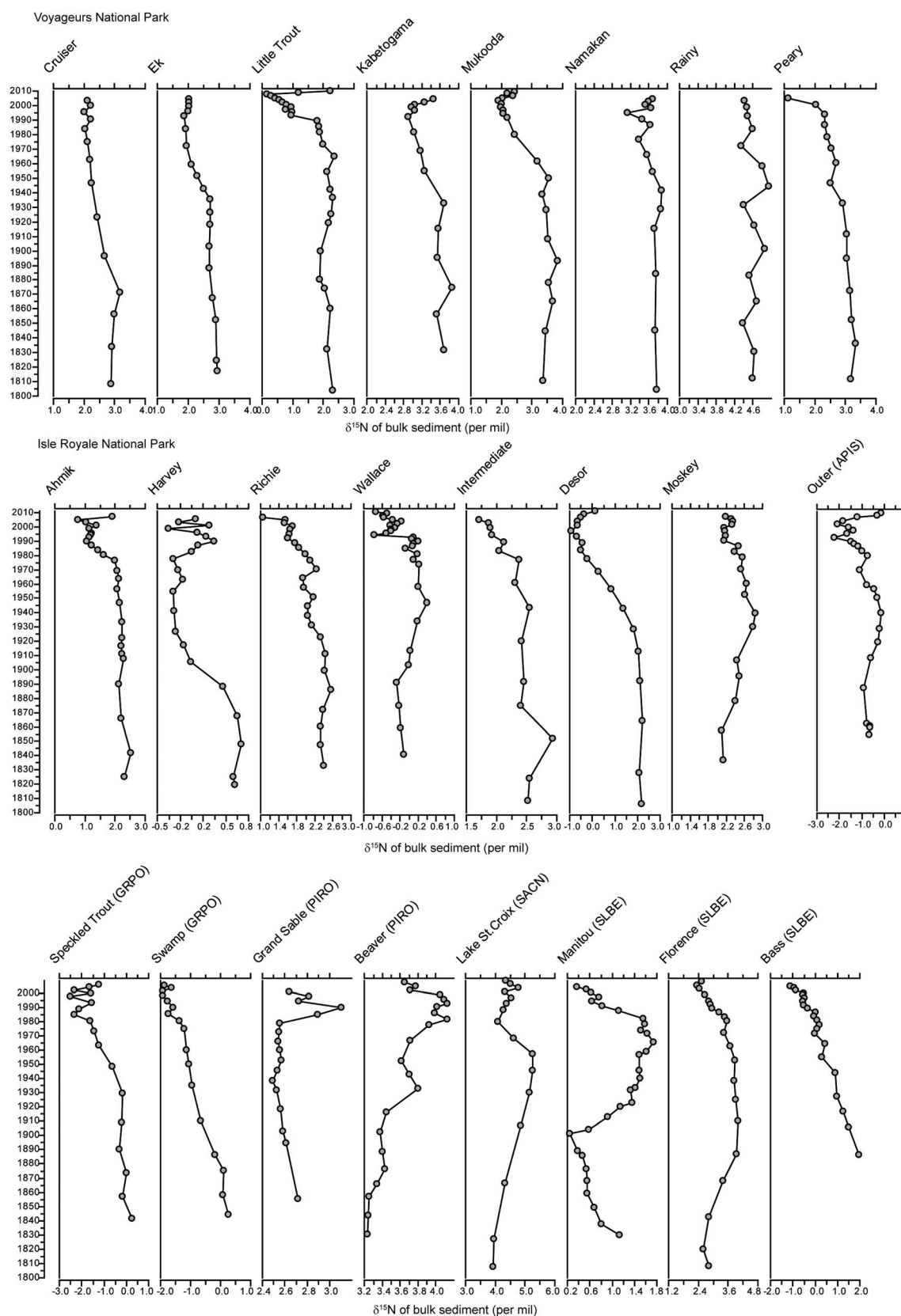


Figure 4. Sediment $\delta^{15}\text{N}$ profiles for all the study lakes, except lakes with duplicate cores (Tettegouche, August, and Nipisiquit).

There is not a strong interannual correlation among the NADP sites; however, the decreasing trend in atmospheric DIN deposition in recent years can be seen at many of the sites (Figure 1). Over the period of NADP monitoring there has been a transition from NO_3 dominating the Nr deposition, to deposition of NH_4 being higher (Figures S2 and S3). It is unclear whether this transition in the predominant form of inorganic Nr has impacted the isotopic ratio of DIN deposition. The assessment of the $\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{15}\text{N}\text{-NH}_4$ in precipitation is a large data gap for this region. The opposing trends in NO_3 and NH_4 yield an overall trend in inorganic nitrogen deposition that appears to have changed very little over the period of record.

3.5. Climatic Factors and Lake Thermal Properties

The MINLAKE model was used to describe the temperature-depth relationships in four of our study lakes from 1962 to 2011 (Cruiser and Little Trout, Voyageurs NP, and Siskiwit and Richie, Isle Royale). The model performed well for deep lakes but was not useful for shallow lakes (e.g., Wallace and Ahmik Lake, Isle Royale) where prolonged periods of stratification were not observed. The modeled parameter, duration of stratification (in days), was found to be the most sensitive to weather [Edlund *et al.*, 2014]. The duration of stratification in lakes on Isle Royale show a variable response to weather. Both lakes experienced prolonged periods of stratification in the late-1990s and a steadily increasing period of open water each year (Figure 5). The lakes in Voyageurs have very similar trends in thermal properties with a peak in the duration of stratification in early the 2000s, and a bimodal trend in length of open water with peaks in the early 1980s and early 2000s.

3.6. Algal Paleoecology

Diatom records for 19 of the study lakes are described in detail in previous publications (references in Table 1) and are summarized only briefly here. Wallace Lake, which is a new record, is presented in more detail. Diatom community turnover, including zones with significant shifts, is included for individual lakes in the supporting information (Figure S4). In general, lakes from Voyageurs show a fairly consistent trajectory of community turnover through time with some evidence of very recent changes (circa 1990) in the diatom communities (Figure 6). Turnover of diatom assemblages in lakes on Isle Royale was minimal (stable) up to the early 1900s, followed by minor changes up to approximately 1950, then a period of greatest turnover between 1950 and ~1970 and becoming more stable thereafter (Figure 6). Lakes at Sleeping Bear Dunes show much greater turnover in their diatom communities than that in the other parks, especially during the period of 1900 to 1950, when land clearance and small-scale farming briefly took hold. The lakes in Pictured Rocks and Apostle Islands show a consistent, steadily changing diatom turnover over the last ~150 years.

The subfossil diatom record for Wallace Lake is similar to many of the other shallower lakes in the data set, where benthic species predominate (Figure S5) [Edlund *et al.*, 2011]. The planktonic species which appear in Wallace Lake after ~1920 (*Cyclotella michiganiana* and *Discostella stelligera*) are true euplankton and would suggest the presence of a defined epilimnion for at least part of the summer and possibly an increasing N:P supply [Saros and Anderson, 2015] (Figure S5). Also, after 1920 chrysophytes increase, further suggesting a planktonic environment and increase in dissolved organic matter [Daggett *et al.*, 2015]. This shift in the diatom communities at around 1920 is the most significant one over the last 170 years, with another minor shift taking place around 2000. The later shift is characterized more by changes in the benthic and tychoplanktonic communities amongst generalist taxa (e.g., *Staurosira construens*).

Many of the diatom records contain taxa that are known to respond to nutrient additions, N in particular [Saros *et al.*, 2005; Daggett *et al.*, 2015]. *Fragilaria crotonensis*, *Asterionella formosa*, and *Tabellaria flocculosa* are all examples of indicator taxa that have responded positively to in situ experimental nutrient additions. All but four lakes (Outer Lagoon, APIS; Florence Lake, SLBE; Wallace Lake, ISRO; and Harvey Lake, ISRO) contained at least one of these indicator taxa, and half of them contained two or more (Table S1).

4. Discussion

4.1. Correlation of NADP Data and Lake Sediment Nitrogen Isotopes

Ten out of 28 lakes (36%) were found to have a relationship between bulk sediment $\delta^{15}\text{N}$ and some form of annual inorganic nitrogen (total, NO_3 , or NH_4) deposition (kg ha^{-1}) (Figure 7). N isotopes in some lakes were correlated with more than one N form (Table 2). Four (14%) were found to have a significant negative relationship between sediment $\delta^{15}\text{N}$ and total atmospheric DIN deposition, while in seven others (25%) $\delta^{15}\text{N}$ was significantly correlated with NH_4^+ with an additional two lakes having strong negative relationships

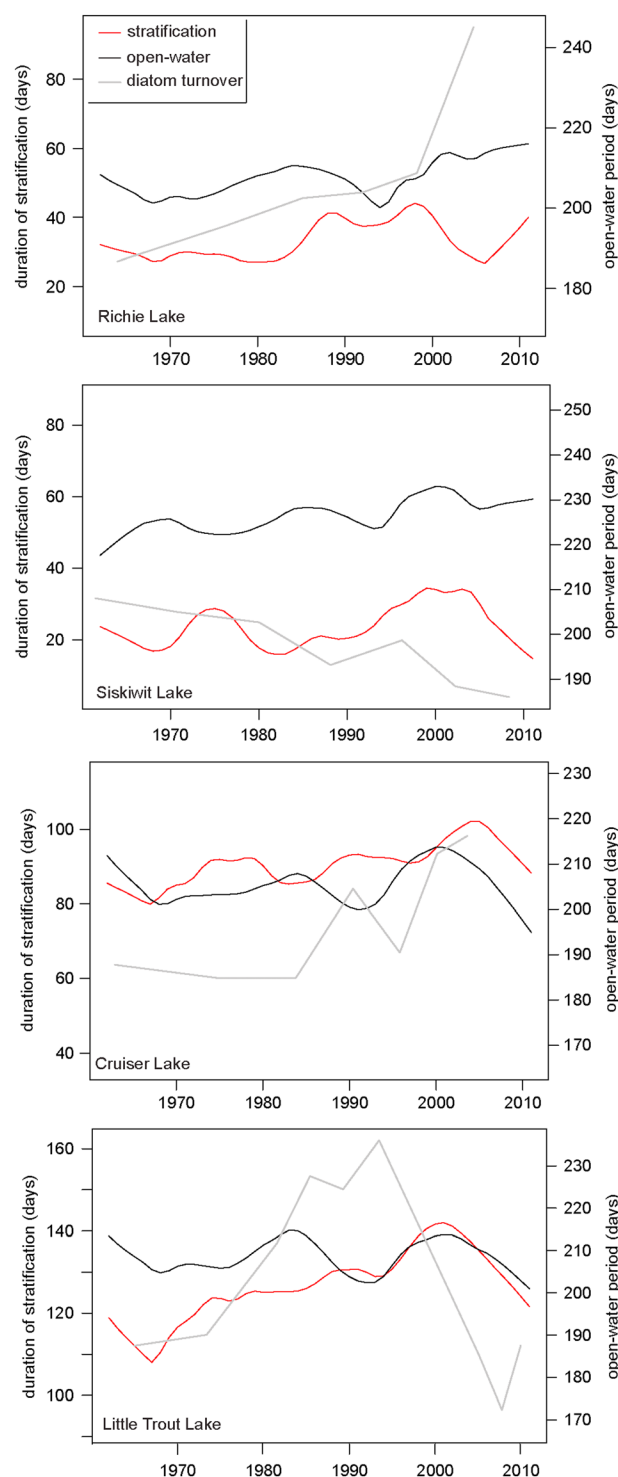


Figure 5. Modeled thermal properties of two lakes in Isle Royale (Richie and Siskiwit) and two in Voyageurs (Cruiser and Little Trout). Black line is the duration of open water (days), red line is the duration of stratification (days), and grey line is the diatom DCA axis 1 trend superimposed on the graph (shown as unitless).

($p < 0.1$). Atmospheric nitrate deposition was significantly correlated with bulk sediment $\delta^{15}\text{N}$ in four of the lakes (14%). These findings suggest that the nitrogen isotopic signature of atmospheric DIN deposition preserved in the sediments of northern lakes is highly variable.

In lakes where $\delta^{15}\text{N}$ is correlated with atmospheric DIN deposition, the relationship is negative, with greater deposition reflecting a more depleted isotopic signature (Figure S6). Recent work by Geng *et al.* [2014] suggests that the changes in acidity of the atmosphere from inputs of anthropogenic N and S may yield a more depleted $\delta^{15}\text{N}\text{-NO}_3$ due to influences on the atmospheric partitioning of NO_3 from gas to aerosol phase. In addition, depleted sources of N from fossil fuel combustion and agricultural activities (such as the use of anhydrous ammonia as a fertilizer) can contribute directly to a more depleted atmospheric DIN pool [Nanus *et al.*, 2008; Ellis *et al.*, 2013; Walters and Goodwin, 2015]. The $\delta^{15}\text{N}\text{-NO}_3$ in precipitation has been shown to reflect NO_x sources and has been found to range between -7 and $+2\text{‰}$ [Elliott *et al.*, 2007; Nanus *et al.*, 2008]. We found that $\delta^{15}\text{N}\text{-NO}_3$ in precipitation collected at Isle Royale and the north shore highlands of Lake Superior ranged from -5 to 0‰ based on limited sampling in 2014 (D. Toczydlowski, unpublished data, 2015). The negative relationships we find in some lakes suggest that greater atmospheric deposition of an isotopically depleted DIN yields a more depleted bulk sediment $\delta^{15}\text{N}$ (Figure S6).

The lakes with sediment $\delta^{15}\text{N}$ records that correlate with atmospheric DIN deposition are located in three main areas: Isle Royale, Apostle Islands, and the Lake Superior highlands of Minnesota. Few or no lakes in Pictured Rocks, Voyageurs, and St. Croix, which have higher atmospheric DIN loads (Figure 1), exhibit a relationship between DIN deposition and sediment $\delta^{15}\text{N}$. We suspect that these regional differences result from a combination of atmospheric N deposition patterns, physical factors (e.g., watershed area), lake nutrient limitation, and local hydrology (including lake water residence time). Each of these factors ultimately influences or is influenced by the

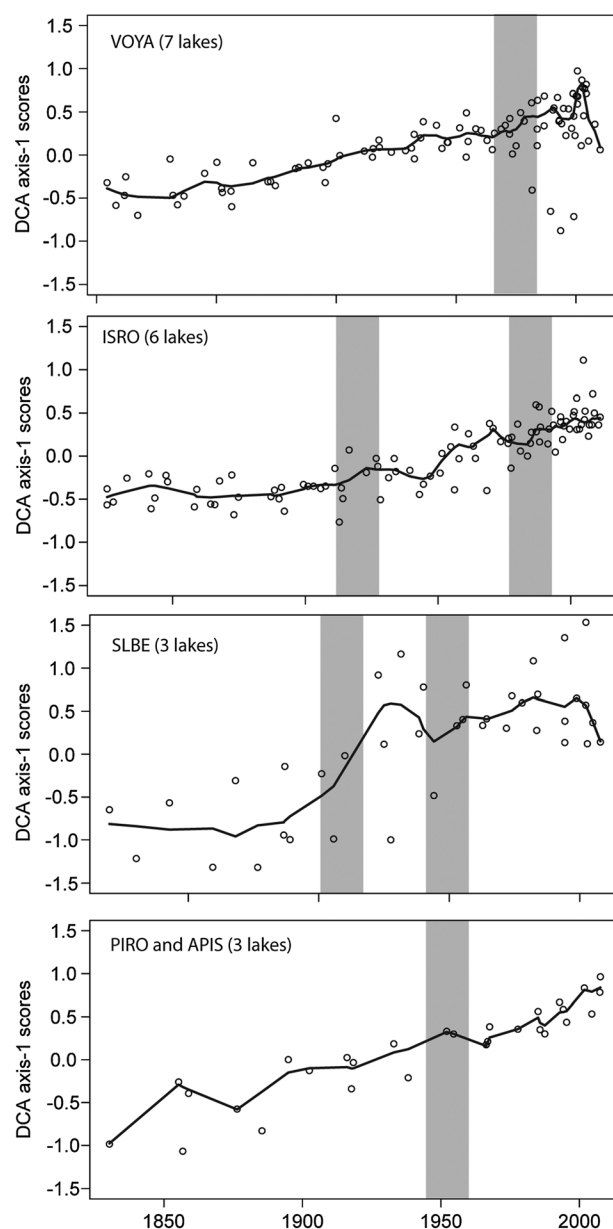


Figure 6. DCA axis 1 scores for all 19 lakes with diatom paleoecological records. Loess smooth curve for each park area shows the general trend of diatom community turnover through time. Shaded bars represent the timing of significant shifts in the diatom assemblages (details in the supporting information).

stream NO_3 [Houlton and Bai, 2009; Mnich and Houlton, 2015]. Greater DIN deposition would promote higher fractionation in watershed soils, and therefore, a more enriched $\delta^{15}\text{N}$ NO_3 would leach from the forest soils. Conversely, with less DIN deposition there is greater N retention in the soils and less fractionation yielding a more depleted $\delta^{15}\text{N}$ - NO_3 . Previous sediment core studies of long-term nitrogen cycling in forested landscapes have found that greater N availability yields a more enriched lake sediment $\delta^{15}\text{N}$ [Hu et al., 2001; McLauchlan et al., 2007]. Furthermore, Canham et al. [2012] suggest that lakes with large watershed to lake area ratios would be more susceptible to N saturation (from high Nr deposition), owing to a greater area of forested land contributing N. In the Voyageurs lakes, which generally do not show a relationship between sediment $\delta^{15}\text{N}$ and Nr deposition trends, the water column has higher DIN concentrations and the watershed to lake area ratio is generally high (Table 1). We find that the $\delta^{15}\text{N}$ of the sediment records from Voyageur

retention of N in the watershed [Stoddard, 1994], which we propose (and discuss below) determines whether Nr deposition is recorded in the lake sediment $\delta^{15}\text{N}$.

4.2. Influence of Critical Loads and Watershed Nitrogen Retention on Sediment $\delta^{15}\text{N}$

The concept of a critical load of Nr for ecosystems pertains to the threshold where detrimental ecological effects begin to take place compared with the current understanding of the ecosystem. The critical loads for Northern Forests that dominate the study area range from 5 to $7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ [Pardo et al., 2011], which is equivalent to measured rates of Nr deposition in the Lake Michigan region. The implication is that study lakes in the high deposition areas potentially exceed critical loads or are in the later stages of watershed N loss (in the sense of Stoddard [1994]), which would lead to much less Nr retention in the watershed. Our sediment core results suggest that sediment $\delta^{15}\text{N}$ best reflects DIN deposition in lakes that are in watersheds with lower Nr deposition and high nitrogen retention.

The passage of Nr through a forested watershed will clearly impact the isotopic signature of both DIN and organic N being exported to lakes. The proportion of atmospherically derived DIN that is unprocessed and exported from forests can be quite variable and seems to depend on the hydrologic and topographic characteristics of the watershed [Rose et al., 2015]. The greatest fractionation is likely to be during the rate-limiting steps of the N cycle [Kendall et al., 2007]. Previous studies have shown that microbial processing (e.g., nitrification) of DIN in soils and subsequent $\delta^{15}\text{N}$ of soil can closely reflect the $\delta^{15}\text{N}$ of

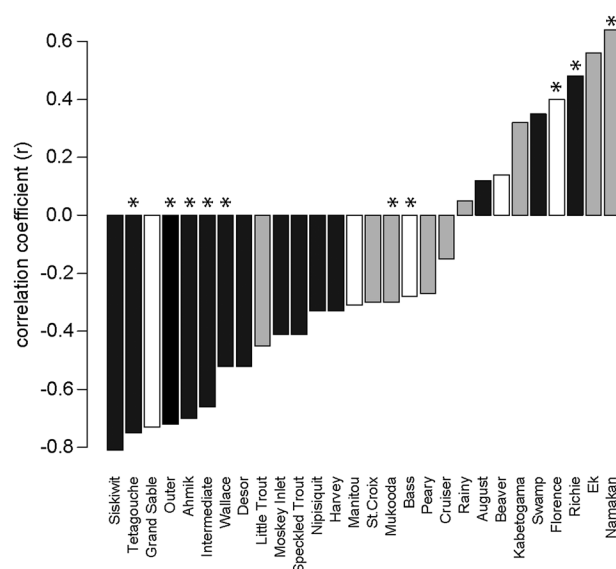


Figure 7. Barplot of the correlation coefficients for annual Nr deposition (total) and sediment $\delta^{15}\text{N}$. Black bars are lakes in the vicinity of western Lake Superior (ISRO, greater MN, and nr GRPO), grey bars are lakes in VOYA, and white bars are lakes in vicinity of Upper Michigan (SLBE and PIRO). Asterisks represent statistical significance between any form of Nr deposition and sediment $\delta^{15}\text{N}$.

accordance with Rayleigh distillation the $\delta^{15}\text{N}$ of the DIN pool will resemble the initial source when it is consumed [Kendall *et al.*, 2007]. Our data suggest that lakes in watersheds with low Nr deposition, high watershed N retention, and resulting N limitation in the lake water column, preserve a sediment $\delta^{15}\text{N}$ that reflects DIN deposition.

Lastly, we have focused on the deposition and passage of DIN through the watershed; however, organic N (dissolved N_{org} or particulate N_{org}) is likely to be as important or possibly greater in proportion for the N inputs to lakes. With no data available for the study watersheds on $\delta^{15}\text{N}_{\text{org}}$ and fractionation, we can only speculate as to the processes that might affect the N_{org} that ends up in the lake. Stottlemeyer and Toczydlowski [2006] found that similar processes likely mediate the output of DIN and DON from the watershed, which suggests a similar rate-limiting step in the cycling of N in the soils and therefore similar fractionation steps. In the lake, the assimilation of DIN by aquatic producers carries a small enrichment factor; however, denitrification of organics in the bottom sediments can have a much greater fractionation [Talbot, 2001]. Ultimately, what we are measuring as the bulk sediment $\delta^{15}\text{N}$ is organic N which is either allochthonous (e.g., watershed soils and plant debris) or autochthonous (e.g., algal or microbial biomass). By explicitly testing the diagenetic environment in three of our lakes and confirming that the primary trend of $\delta^{15}\text{N}$ in bulk sediment is preserved, we have established that postdepositional mineralization of organic N does not shape our records.

4.3. Wallace Lake Nitrogen Biogeochemistry

The biogeochemistry of the Wallace Lake watershed on Isle Royale has been intensively studied since 1982 [Stottlemeyer *et al.*, 1998]. There has also been a precipitation-monitoring station within the watershed since 1983 (formerly station MI97). There has been a decrease in atmospheric inputs of DIN over time. Data from this station show a significant correlation between atmospheric DIN load and the sediment $\delta^{15}\text{N}$ record of Wallace Lake (Figure 8; $n = 15$; $r = -0.52$; $p = 0.045$).

Based on the flow-weighted annual concentrations of $\text{NO}_3\text{-N}$ in the inflow to Wallace Lake and the nearby precipitation station, atmospheric DIN does not appear to drive the concentrations of $\text{NO}_3\text{-N}$ leaving the watershed. Rather, $\text{NO}_3\text{-N}$ trends are controlled by the indirect effects of climate on watershed biogeochemistry—in particular, the net soil-N mineralization rates that are influenced by subsurface hydrology during snowmelt [Stottlemeyer *et al.*, 1998]. This shallow subsurface flow has been shown to be a major factor

lakes is more enriched, suggesting a greater influence of watershed-mediated DIN which possibly erodes the signature of atmospheric DIN deposition.

In forested regions there is generally higher stream NO_3 concentrations in areas where atmospheric DIN deposition is elevated [Rose *et al.*, 2015]. Measured water column DIN concentrations in the study lakes broadly reflect the spatial patterns of Nr deposition (e.g., low at Isle Royale and Apostle Islands; Table 1). N limitation has been confirmed in a number of lakes on Isle Royale [Daggett *et al.*, 2015], indicative of lower deposition of Nr to the watershed and minimal export to the lakes. In watersheds where retention is high, the influence of direct DIN deposition to the lake surface on water column $\delta^{15}\text{N}$ would be greater. Canham *et al.* [2012] showed that direct Nr deposition accounted for a higher proportion of total N input to lakes with high watershed N retention. When available DIN is limiting, there is less fractionation and in

Table 2. Correlation Coefficients Between NADP Data, Diatom Turnover, and Sediment $\delta^{15}\text{N}$

Lake	Park	Correlation Coefficient $\delta^{15}\text{N}$ -DIN	Correlation Coefficient $\delta^{15}\text{N}$ - NH_4	Correlation Coefficient $\delta^{15}\text{N}$ - NO_3	Correlation Coefficient $\delta^{15}\text{N}$ -DCA axis 1
Outer Lagoon	APIS	-0.72**	-0.56**	-0.72**	0.2
Tetagouche Lake	greater MN	-0.75**	-0.86**	-0.094	ns
August	greater MN	0.12	-0.022	0.35	ns
Nipisiquit	greater MN	-0.33	-0.11	-0.54	ns
Harvey Lake	ISRO	-0.33	-0.28	-0.27	0.62**
Richie Lake	ISRO	0.48	0.23	0.78**	-0.83**
Wallace Lake	ISRO	-0.52**	-0.22*	-0.49*	-0.37
Desor Lake	ISRO	-0.52	-0.49	-0.45	-0.89**
Intermediate Lake	ISRO	-0.66	-0.85**	0.018	ns
Ahmik Lake	ISRO	-0.7**	-0.66**	-0.65**	-0.78**
Lake Superior, Moskey Inlet	ISRO	-0.41	-0.25	-0.52	ns
Siskiwit Lake	ISRO	-0.81	-0.99*	0.94	-0.83**
Swamp Lake	nr GRPO	0.35	0.46	0.25	ns
Speckled Trout Lake	nr GRPO	-0.41	-0.47	-0.36	ns
Grand Sable	PIRO	-0.73	-0.69	-0.76	0.48
Beaver Lake	PIRO	0.14	-0.17	0.55	-0.76**
Lake St. Croix 6B	SACN	-0.3	-0.44	-0.13	ns
Bass Lake	SLBE	-0.28	-0.61**	0.15	0.83**
Lake Manitou	SLBE	-0.31	-0.56	0.016	0.47
Florence Lake	SLBE	0.4	-0.81**	0.68	-0.37
Cruiser Lake	VOYA	-0.15	-0.01	-0.34	-0.81**
Ek Lake	VOYA	0.56	0.6	0.41	0.8**
Peary Lake	VOYA	-0.27	-0.64	0.43	-0.94**
Namakan Lake	VOYA	0.64	0.76**	0.35	-0.49**
Kabetogama Lake	VOYA	0.32	0.5	-0.07	-0.77**
Rainy Lake	VOYA	0.05	-0.12	0.36	-0.24
Little Trout	VOYA	-0.45	-0.36	-0.38	-0.06
Mukooda Lake	VOYA	-0.3	0.069	-0.68**	ns ^a

*Statistical significance of $p < 0.1$.**Statistical significance of $p < 0.05$.^ans = not sampled.

controlling NO_3 contributions, and solutes, in general, (e.g., dissolved organic carbon and dissolved organic N) to Wallace Lake and lakes in similar northern watersheds [Stottlemeyer and Toczydlowski, 2006; Rose et al., 2015]. In addition, preliminary isotopic data ($\delta^{18}\text{O}$ and $\delta^{15}\text{N}$) on stream NO_3 -N suggest that the main source is snow-melt and contributions from riparian alder (Toczydlowski, unpublished data). What this has meant for Wallace Lake is an increase in volume-weighted NO_3 -N concentrations over time.

There is a coincident shift in both NO_3 concentration and $\delta^{15}\text{N}$ at ~ 1995 , with sediment $\delta^{15}\text{N}$ becoming more depleted and both NO_3 and sediment $\delta^{15}\text{N}$ becoming more variable (Figure 8); there is no significant relationship between inflow NO_3 -N concentrations and sediment $\delta^{15}\text{N}$ at finer (interannual) timescales. This coincident shift in NO_3 concentrations and sediment $\delta^{15}\text{N}$ is more likely a result of changes in the timing and amount of subsurface flow. Indeed, the reduction in surface runoff over time increases the probability that a higher fraction of water entering the lake is from subsurface flow. This finding adds validity to our speculation that in watersheds with high N retention and substantial subsurface flow, the resulting $\delta^{15}\text{N}$ -DIN is depleted. Overall, the N retention characteristics of the Wallace Lake watershed conform to the early stages described by Stoddard [1994] [Stottlemeyer and Toczydlowski, 2006; Stottlemeyer et al., 1998]. It appears that the sediment $\delta^{15}\text{N}$ record in Wallace Lake reflects both the N from direct deposition to the lake surface and contributions from the watershed.

4.4. Long-Term Nitrogen Cycling in Northern Lakes

Of the 28 lakes in this study, 14 exhibit a sedimentary profile showing a gradual depletion of sediment $\delta^{15}\text{N}$ beginning in the midtwentieth century, which is similar to other lake sediment records from North America [Holtgrieve et al., 2011]. This trend is also consistent with human alteration of the global composition and concentration of atmospheric nitrogen (Figure 9) [Hastings et al., 2009]. While the specific mechanisms

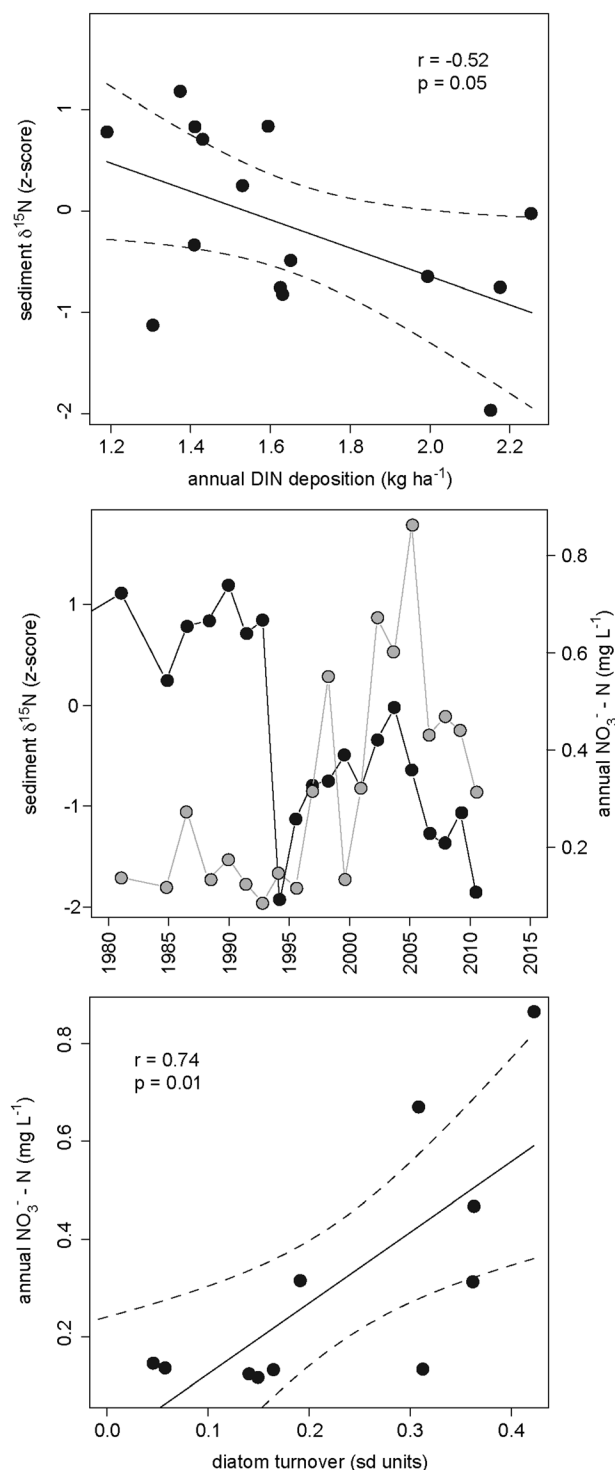


Figure 8. Wallace Lake sediment core and watershed biogeochemistry. (top) relationship between sediment $\delta^{15}\text{N}$ and total annual N_r deposition. (middle) Measured flow-weighted NO_3^- discharge from Wallace Lake (grey circles) and sediment $\delta^{15}\text{N}$ (black circles). (bottom) Relationship between measured flow-weighted NO_3^- discharge from Wallace Lake and diatom community turnover.

controlling the isotopic composition of atmospheric DIN are not fully understood [Geng *et al.*, 2014], it is likely driven by human alterations to global cycles of both N and S (in the sense of Galloway *et al.* [2003]) which influence atmospheric acidity.

In a study by Holtgrieve *et al.* [2011] 25 out of 33 lakes (76%) preserved a long-term sediment $\delta^{15}\text{N}$ record similar to that found in the Greenland Summit ice core which showed a depletion of NO_3^- - $\delta^{15}\text{N}$ beginning in the midtwentieth century [Hastings *et al.*, 2009]. In those lakes from Holtgrieve *et al.* [2011] that were temperate or boreal, half (5 of 10) had a sediment $\delta^{15}\text{N}$ record similar to the Hastings *et al.* [2009] ice core record. Such profiles of $\delta^{15}\text{N}$ have been cited—along with other indicators of human alteration of global biogeochemical cycles—as evidence for the onset of the Anthropocene [Wolfe *et al.*, 2013]. Similar to the work of Holtgrieve *et al.* [2011], we find that 52% of our northern lake data set exhibits the characteristic profile of the Anthropocene.

In areas of high N_r deposition where the critical load has been approached or exceeded, the assimilative capacity of the watershed for N_r has been reduced. The deposition rates across our study region are sufficient to induce ecological changes in both terrestrial [Pardo *et al.*, 2011] and aquatic ecosystems [Baron *et al.*, 2011; Saros *et al.*, 2011]. In a modeling exercise, Ellis *et al.* [2013] found that the Northern Forests ecoregion of the Great Lakes is currently in excess of published critical N_r loads. This raises the question of whether the sediment $\delta^{15}\text{N}$ record, be it driven directly by atmospheric N_r or not, might also be related to ecological changes in lakes?

4.5. Algal Change in Lakes

We find that sediment $\delta^{15}\text{N}$ correlates with diatom turnover (as DCA axis 1 scores) in 12 of the 19 lakes (63%) for which we have diatom records. Only five of these lakes (25%) have $\delta^{15}\text{N}$ records that correlate with some form of atmospheric DIN load. We propose three possible scenarios under which N_r inputs might correlate with turnover in diatom communities: (1) systems dominated by direct atmospheric deposition of N_r to the lake surface (high

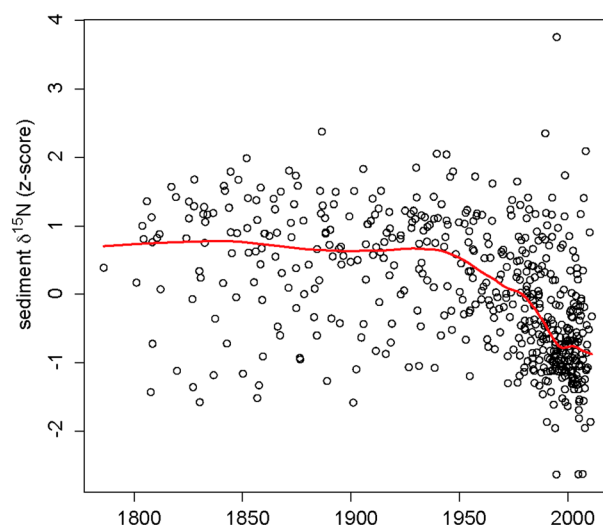


Figure 9. Sediment $\delta^{15}\text{N}$ from all cores standardized as z scores. Loess smooth curve in red.

watershed N retention), (2) systems with high deposition of atmospheric Nr and leakage of Nr from the watershed (low watershed N retention), and (3) systems with active in-lake sequestration of atmospheric N_2 by cyanobacteria. Furthermore, N is not the sole contributing nutrient to algal turnover in lakes, and the role of phosphorus (P) cycling is equally important. Recent in situ nutrient enrichment experiments in lakes on Isle Royale have also found that *F. crotonensis* and *Asterionella formosa* respond to P additions as well as N [Daggett et al., 2015]. Certainly, the role of P is paramount in the growth of cyanobacteria [Schindler, 2012]. We also acknowledge the role that climate variability may have on internal P cycling due to changes in water column stratification and oxygen demand [Hupfer and Lewandowski, 2008]

and the direct effect that changes in stratification can have on diatom communities [Rühland et al., 2015]. Therefore, we cannot ignore the possible interactive stresses that climate variability and nutrient (N and P) inputs have on the aquatic ecosystem [Baron et al., 2013].

4.5.1. High Watershed N Retention

In Ahmik Lake on Isle Royale, total DIN, NO_3 , and NH_4 deposition and diatom turnover (DCA axis 1 scores) all correlate with the sediment $\delta^{15}\text{N}$ (Table 2). Ahmik Lake has a small surface area, shallow depth and low water column DIN. Because of the shallow depth, there is not a strong planktonic community [Edlund et al., 2011]. However, a notable shift in diatom assemblages in the late 1970s involves an increase in *Fragilaria crotonensis*, a species that responds strongly to N additions [Saros et al., 2005]. This diatom shift also correlates with the marked depletion in sediment $\delta^{15}\text{N}$. Similarly, Bass Lake at Sleeping Bear Dunes, where NH_4^+ deposition correlates with sediment $\delta^{15}\text{N}$, the diatom assemblages contain *Asterionella formosa* and *F. crotonensis*, the former also responding strongly to N additions [Saros et al., 2005]. In general, the presence of indicator diatom species with high N requirements (Table S1) in those lakes with a sediment $\delta^{15}\text{N}$ record correlated with diatom turnover and Nr deposition (~25% of the lakes) supports the observation that atmospheric inputs can play a role in algal shifts.

There is no relationship between sediment $\delta^{15}\text{N}$ and the diatom turnover in Wallace Lake. However, the increase in $\text{NO}_3\text{-N}$ concentrations in the lake is significantly correlated with diatom turnover in the lake (Figure 8; $r = 0.74$; $p = 0.01$). This relationship suggests that watershed inputs of NO_3 —or possibly both N and P—are driving changes in community composition of the diatoms in Wallace Lake. Thus, while the isotopic signature of the atmospheric DIN appears preserved in the lake sediment record, the diatom community turnover is mediated to a greater degree by nutrient inputs from the watershed. Given the previous work of Stottlemeyer and Toczydlowski [2006], it appears that climatic changes that affect the transport of NO_3 from the watershed via shallow subsurface hydrology are an important factor indirectly influencing diatom community change. Furthermore, given that the diatom communities also show an increase in planktonic cyclotelloids, it is possible that some portion of diatom turnover is attributable to the direct effects of climate on lake thermal properties [Rühland et al., 2015].

4.5.2. Low Watershed N Retention

Many of the lakes in this study exhibit a relationship between long-term diatom turnover and sediment $\delta^{15}\text{N}$ but show no evidence that Nr deposition is significantly related to community turnover. It is possible that the input of DIN from the watershed is influencing the sediment $\delta^{15}\text{N}$ record, while both N and P from the watershed would influence a portion of the variability in diatom assemblages. The majority of the lakes in Voyageurs are a good example of the influence of watershed DIN. The sediment $\delta^{15}\text{N}$ records from this region are enriched relative to others, suggesting ample nitrogen availability [Hu et al., 2001], and four of the six lakes

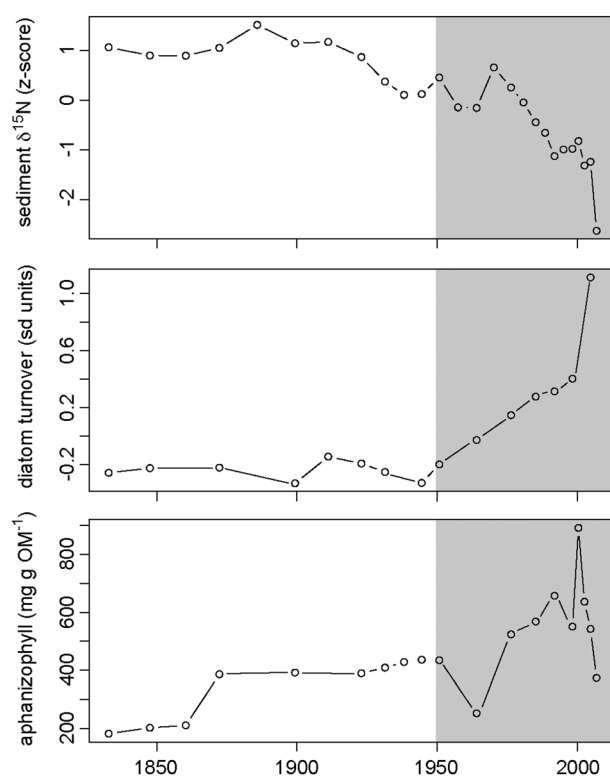


Figure 10. Sediment profiles from Richie Lake on Isle Royale National Park, Michigan. (top) Sediment $\delta^{15}\text{N}$ profile over time; gray shaded area post-1950. (middle) Diatom community turnover as DCA axis 1 scores over time (SD units). (bottom) Biomarker of N_2 -fixing cyanobacteria over time; aphanizophyll carotenoid in sediment organic matter.

with diatom records show significant correlations of sediment $\delta^{15}\text{N}$ with diatom turnover (but no correlation with atmospheric N_r deposition). We are not including Namakan Lake in Voyageurs in the six lakes with diatom records (Table 2) because it has been shown that hydrologic changes from damming this lake likely impacted the diatom communities [Serieyssol *et al.*, 2009].

4.5.3. Fixation of Atmospheric N_2

An alternative explanation for the correlation between diatom turnover and sediment $\delta^{15}\text{N}$ is that the algal communities themselves are processing and fractionating incoming DIN. Algae that have the ability to fix atmospheric N_2 , i.e., the heterocystous cyanobacteria, can directly impact the N supply to lakes and thereby alter sediment $\delta^{15}\text{N}$ [Patoine *et al.*, 2006]. The abundance of this type of algae can be detected in sediment records through the analysis of sedimentary pigments. In Richie Lake on Isle Royale, cyanobacteria blooms have been observed in recent years, an increase that is corroborated by the presence of carotenoids of bloom-forming and N_2 -fixing cyanobacteria in the sediment record (Figure 10). Moreover, there is a strong relationship between the cyanobacterial carotenoid, aphanizophyll, which is characteristic of N_2 fixers, and the sediment $\delta^{15}\text{N}$ (Figure 10; $r = -0.54$; $p = 0.02$). There is also a very strong relationship between aphanizophyll and the diatom turnover (Figure 10; $r = -0.83$; $p < 0.001$), suggesting a common nutrient driver (P) for both cyanobacteria and diatoms, or alternatively that N fixed by cyanobacteria is impacting diatom community turnover [Cottingham *et al.*, 2015]. Notable are diatom species (*Asterionella formosa* and *Fragilaria crotonensis*) that are able to capitalize on the addition of N_r to the lake nitrogen pool via N_2 fixation. Similar relationships between sediment $\delta^{15}\text{N}$ and diatom turnover are present in Desor Lake ($r = -0.89$; $p < 0.001$), where sediment $\delta^{15}\text{N}$ does not appear to be related directly to measured N_r deposition and colonial cyanobacteria have been observed in the lake. Richie and Desor lakes highlight how the algal communities can shape the sediment $\delta^{15}\text{N}$ record. Similar observations have been made in previous work from southern Saskatchewan, Canada, where a strong linear relationship between sedimentary pigments and $\delta^{15}\text{N}$ were attributed to N_r fixation by algae [Leavitt *et al.*, 2006].

4.5.4. Lake Thermal Properties and Diatom Community Turnover

As acknowledged earlier in this section, nutrient inputs alone are not responsible for all the observed shifts in diatom communities over time. Studies from this region have found that the direct influence of climate on lake thermal properties can impact the structure of diatom communities [Saros *et al.*, 2012; Rühland *et al.*, 2010, 2015]. The primary mechanism for this influence is the link between air temperature and stratification and mixing of the lake water column, where a prolonged period of stratification promotes an abundant planktonic habitat and changes in mixing depth favor certain planktonic diatom species. The previous work by Edlund *et al.* [2014] found that weather had the greatest influence on the duration of stratification in lakes of this region. When we compare the duration of lake stratification and the number of ice-free days in a year to the diatom DCA axis 1 scores for four of our lakes, we do not find any significant relationships. We acknowledge that the number of samples is low ($n = 6$) in some cases which may impact our analysis. However, there are coincident shifts in the diatom communities during periods of changes to the thermal properties (Figure 5). In Richie Lake there is a weak positive relationship between DCA axis 1 scores and duration of stratification

($r = 0.79$; $p = 0.06$) suggesting that periods of prolonged stratification have an influence on structuring diatom assemblages. It is also possible for lake stratification to influence internal nutrient loading which may in turn impact diatom communities. While lake thermal properties do not appear to be a strong predictor of diatom community turnover in the four lakes tested, further work may reveal a more useful trend across the region.

5. Conclusions

Our study suggests that about 36% of lakes in these western Great Lakes parks of the U.S. preserve a sedimentary record of $\delta^{15}\text{N}$ that reflects measured Nr deposition. An observable relationship between bulk sediment $\delta^{15}\text{N}$ and measured Nr deposition appears to rely on watershed N retention. There are two scenarios of watershed N retention and associated interpretations of the sediment $\delta^{15}\text{N}$ record: (1) if the watershed has high N retention, Nr deposition is below a critical load, and the water column is N limited—a correlation between Nr deposition and sediment $\delta^{15}\text{N}$ may be observable; and (2) if the watershed has low N retention, Nr deposition exceeds critical load, and the lake has a relatively enriched bulk sediment $\delta^{15}\text{N}$ —there is unlikely to be a correlation between Nr deposition and sediment $\delta^{15}\text{N}$. In regions of high N retention, and climatic changes can also affect the transport of NO_3 from the watershed via shallow subsurface flow, highlighting how two ecosystem stressors may interact with one another.

The correlation of lake algal communities with sediment $\delta^{15}\text{N}$ —whether influenced by atmospheric Nr to the lake surface, watershed inputs, or N_2 fixers—is significant in the majority (63%) of our study lakes. We propose scenarios that describe the various Nr inputs: (1) direct deposition of Nr to the lake and shallow subsurface flow from the watershed, (2) high Nr deposition and indirect inputs of Nr from the watershed, and (3) active sequestration and fixation of atmospheric N_2 by cyanobacteria. Given the paucity of long-term records of Nr deposition (pre-NADP), additional research exploring the relationship between Nr deposition and sediment $\delta^{15}\text{N}$, and the contexts in which this relationship is strongest, would be worthwhile.

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