



## Increasing stoichiometric imbalance in North America's largest lake: Nitrification in Lake Superior

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[1] Lake Superior has exhibited a continuous, century-long increase in nitrate whereas phosphate remains at very low levels. Increasing nitrate and low phosphate has led to a present-day severe stoichiometric imbalance; Lake Superior's deepwater  $\text{NO}_3^-:\text{PO}_4^{3-}$  molar ratio is 10,000, more than 600 times the mean requirement ratio for primary producers. We examine the rate of  $[\text{NO}_3^-]$  increase relative to budgets for  $\text{NO}_3^-$  and fixed N. Nitrate in Lake Superior has continued to rise since 1980, though possibly at a reduced rate. We constructed whole-lake  $\text{NO}_3^-$  and N budgets and found that  $\text{NO}_3^-$  must be generated in the lake at significant rates. Stable O isotope results indicate that most  $\text{NO}_3^-$  in the lake originated by in-lake oxidation. Nitrate in the lake is responding not just to  $\text{NO}_3^-$  loading but also to oxidation of reduced forms of nitrogen delivered to the lake. The increasing  $[\text{NO}_3^-]:[\text{PO}_4^{3-}]$  stoichiometric imbalance in this large lake is largely determined by these in-situ processes. **Citation:** Sterner, R. W., E. Anagnostou, S. Brovold, G. S. Bullerjahn, J. C. Finlay, S. Kumar, R. M. L. McKay, and R. M. Sherrell (2007), Increasing stoichiometric imbalance in North America's largest lake: Nitrification in Lake Superior, *Geophys. Res. Lett.*, 34, L10406, doi:10.1029/2006GL028861.

### 1. Introduction

[2] Anthropogenic acceleration of global- and regional-scale nitrogen (N) cycling is widely known [Galloway and Cowling, 2002; Howarth *et al.*, 2002] and is the source of deep concern [Environmental Protection Agency (EPA), 2002; Vitousek *et al.*, 2002]. Long-term records of ecosystem responses to this increased N fertilization, however, are rare. Historic patterns of anthropogenic N release have been estimated by a variety of methods, e.g. [Environmental Protection Agency (EPA), 2000]. Long-term environmental responses to accelerated N release have been hard to distinguish amidst a background of other, simultaneously occurring changes. N accumulation is often obscured by, and related to, multiple human-caused impacts and other long-term trends. It has therefore been said that, "we have a poor understanding of nitrogen's rate of accumulation in environmental reservoirs" [Galloway and Cowling, 2002].

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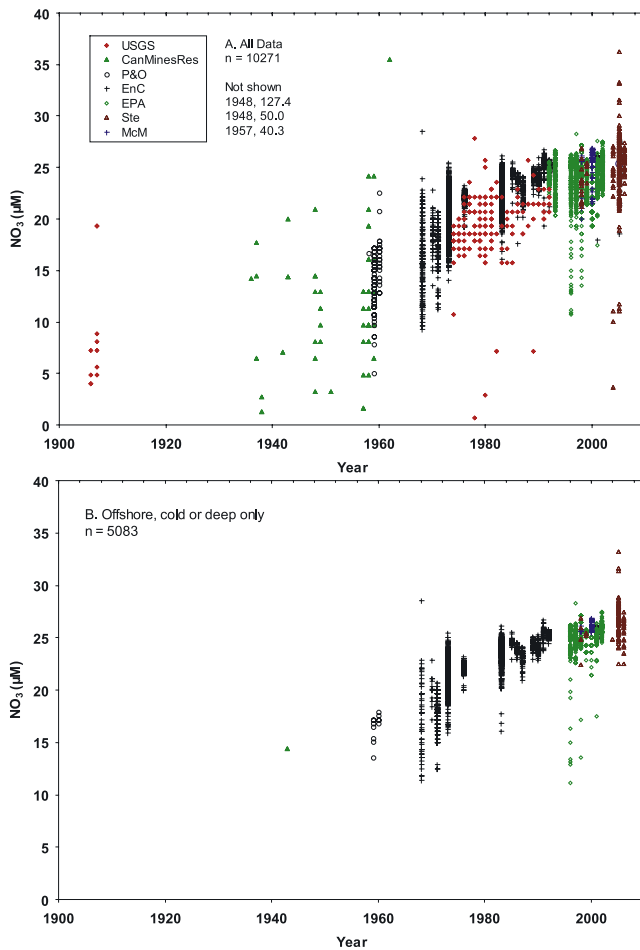
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Here, using a large database for observations of  $\text{NO}_3^-$  concentrations together with a synthesis of mass balance information, we explore the dynamics and causes of a century-long record of environmental N buildup in one of Earth's largest lakes. Besides being a valuable record of the pattern of N accumulation over this past century, these data offer insights into ecosystem response to excess N and stoichiometric N:P balancing mechanisms.

[3] Nitrogen, and often more specifically nitrate ( $\text{NO}_3^-$ ), has been increasing in many aquatic environments downwind from agricultural, urban and industrial activities [Bergström *et al.*, 2005].  $\text{NO}_3^-$  is known to have increased in all the Laurentian Great Lakes [Barica, 1990]. Increasing  $[\text{NO}_3^-]$  in Lake Superior was noted two decades ago [Bennett, 1986; Weiler, 1978; H. Dobson, Nutrients in Lake Superior, unpublished manuscript, 1972, p. 68, Canada Centre for Inland Waters, Burlington, Ontario], but has received little attention since. At that time it was determined that  $[\text{NO}_3^-]$  had increased four-fold between 1906 and 1973, and it was suggested that the trend was exponentially increasing at  $2\% \text{ yr}^{-1}$ . Today,  $\text{NO}_3^-$  is the dominant form of nitrogen in the lake's waters (81% of the total N, according to our recent measurements). Since 1973,  $\text{NO}_x$  emissions in the U.S. have been approximately level [EPA, 2000]. Whether environmental N reservoirs have responded to this leveling is still an open question.

### 2. Methods

[4] We compiled a database of 10,000+ observations of  $[\text{NO}_3^-]$  in Lake Superior and its outflow consisting of all known historical values and many published and unpublished modern values (see Table S1 in the online auxiliary material<sup>1</sup> for more information). Our compilation includes sources referenced by previous work and other, newer sources, including original data (abbreviations in parentheses refer to the legend code of Figure 1). The earliest known measurements (1906–1907, USGS) were taken from the railroad bridge above the Sault Ste. Marie locks on the St. Marys River outflow [Dole, 1909]. Data for the period 1936–43 were reported by the Canada Department of Mines and Resources, Mines and Geology Branch, Bureau of Mines [Leverin, 1947] (CanMinesRes) both from the lake and the outflow. During 1959–60,  $[\text{NO}_3^-]$  was measured during studies contracted by the School of Public Health, University of Minnesota and values were reported in two [Putnam and Olson, 1960, 1961] of several reports (P&O) resulting from that study. In 1968, lakewide monitoring was



**Figure 1.** Long-term trends in Lake Superior  $[\text{NO}_3^-]$ . (a) Entire compilation with data coded by the lab performing chemical analysis. Three off-scale points are indicated in text in the plot and likely are incorrect readings. (b) Filtered data reducing or eliminating seasonal and spatial variability in  $[\text{NO}_3^-]$  (see Methods). Filtered data include deep values and surface values for cold season, offshore. Data coded as in A, above. The symbols represent different laboratories performing the chemical analyses.

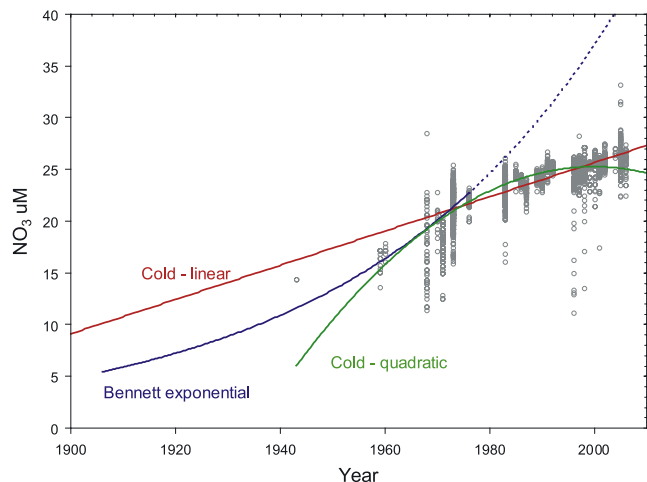
begun by Environment Canada (EnC) and continues to the present; we had data from 1968 to 2001 available to us. The USGS reported nitrate values for the St. Marys River outflow during the period 1974–1992 (USGS). Another large monitoring program was begun by the US EPA (EPA) in 1992. We had data from 1992 to 2002 available to us. Observations from the most recent years included unpublished data from the lab of the first author (Ste) and published data from papers by McManus and coworkers (McM) [Heinen and McManus, 2004; McManus et al., 2003]. Previous to approximately 1960,  $[\text{NO}_3^-]$  was generally measured by the phenoldisulphonic acid, after which studies generally employed Cd reduction using an autoanalyzer. Values from the Ste lab were calculated by comparison to NIST standards; the source of standards used by other laboratories is unknown to us.

[5] Stable isotopes of oxygen in  $\text{NO}_3^-$  were measured in the lake and in potential loading sources. Means for the

water column were calculated from 11 samples collected below 30 m at two sites during 2004–5. Means for precipitation were calculated from samples taken at National Atmospheric Deposition Program (NADP) stations during 2005 together with previously published data from the eastern shore of the lake [Spoelstra et al., 2001]. Samples collected from the lake and at the NADP sites were analyzed for  $\delta^{18}\text{O}_{\text{NO}_3}$  using the bacterial method [Sigman et al., 2001]. Samples were analyzed at the Marine Microbial Biogeochemistry Lab at the Woods Hole Oceanographic Institution. Analytical precision was 0.2%; values are expressed relative to standard mean ocean water (SMOW). For further details, see Finlay et al. [2007].

### 3. Results and Discussion

[6] The nitrate concentration exhibits a continuous buildup, with increases continuing into recent years (Figure 1a). Nitrate in Lake Superior increased from  $\sim 5$  to  $\sim 25 \mu\text{M}$  in one century. It has increased  $\sim 5 \mu\text{M}$  (an additional  $8 \times 10^{11}$  g of N) since the last paper to consider this subject was published [Bennett, 1986]. This unusual record might allow us to relate the temporal patterns of ecosystem response to altered N emissions over this century. Some of the variation around the long-term trend is analytical, and some of it comes from spatial and temporal variation in the lake. Presently,  $[\text{NO}_3^-]$  in surface waters decreases  $\sim 2\text{--}4 \mu\text{M}$  during the stratified period beginning in mid-July, and it is much lower in tributaries emptying into the lake than it is in the lake itself. There are no other broadly consistent spatial or temporal trends we could find in the data. To factor out the spatial and temporal variation in  $\text{NO}_3^-$  over these time scales, we therefore selected for further analysis  $>5000$  observations from: A. Samples taken from  $>50$  m depth, or B. Samples taken from  $<50$  m depth during the unstratified period where bottom soundings were  $>50$  m (i.e. cold-water season, away from shore) (Figure 1b). The earliest observations all failed to meet these restrictions because samples were taken from the shore. To test for changes in rates of buildup, we took a phenomenological approach and examined linear and quadratic models of the accumulation. The



**Figure 2.** Same data as in Figure 1b presented along with several different statistical fits.

**Table 1.** Present Day  $\text{NO}_3^-$  Inputs and Outputs in Lake Waters

Source	Nitrate Flux, $\text{mmol m}^{-2} \text{yr}^{-1}$	Notes	Sources of Information
<i>Inputs</i>			
Direct precipitation onto lake surface	12.5 (wet) 3.9 (dry plus droplet) 17.2 (total)	Equal weightings of rates estimated for the U.S. and Ontario, Canada. National Atmospheric Deposition Program (U.S.) data were first averaged by site. The same proportion of dry and droplet deposition relative to wet deposition is assumed for the U.S. is as reported for Ontario	U.S.: Based on 87 site-years of annual $\text{NO}_3^-$ deposition data from 7 sites in the Lake Superior region ( <a href="http://nadp.sws.uiuc.edu/">http://nadp.sws.uiuc.edu/</a> ) Canada: Rates given by <i>Chen et al.</i> [2000] for Ontario.
Watershed, surface runoff	5.92	Discharge-weighted loading from between 3 and 15 samplings per year for one 24-month period of 70+ tributary inputs in the U.S. and Canada, including all major rivers	<i>International Joint Commission</i> [1979]
Watershed, direct groundwater inputs to lake	0.96	Volumetric groundwater input assumed equal to the “residual” in a recent, detailed hydrologic budget for the lake. That hydrologic input then was multiplied by average groundwater $\text{NO}_3^-$ concentrations in MN and WI	Hydrologic budget [ <i>Lenters</i> , 2004] with groundwater concentrations for the Lake Superior watershed in WI and MN reported by state agencies
<i>Outputs</i>			
Outflow	22.4	Present day concentration ( $26 \mu\text{M}$ ) times hydrologic outflow $70.6 \text{ km}^3 \text{ yr}$	Lake concentration, this study. Outflow, mean for 1948–1999 [ <i>Lenters</i> , 2004].
<i>Net Change</i>			
Buildup	23.4	Coefficient of linear fit	This study

linear model  $[y = (-302.5 \pm 0.2) + (0.1641 \pm 0.002)x]$ , where  $y$  is  $[\text{NO}_3^-]$  in  $\mu\text{M}$  and  $x$  is year,  $\pm\text{SE}$  explained 58% of the variability (Figure 2, red curve). Data collected in recent decades reject the previously suggested exponential trend (Figure 2, blue curve).

[7] Long-term records of regional N emissions in the Lake Superior airshed do not exist. However, at the national level,  $\text{NO}_3^-$  emissions were constant in the U.S. [*EPA*, 2000] and Canada [*Chen et al.*, 2000] in the period 1980–2000, following the large increases that occurred between 1940 and 1980. Incorporating a quadratic term to the model ( $y = (-23800 \pm 700) + (23.856 \pm 0.738)x - (0.005965 \pm 0.000186)x^2$ ), explained 7% more variability, a small but statistically significant ( $P < 0.0001$ ) term (Figure 2, green curve). Further, a linear fit to the post-1980 data exhibits a slower increase ( $y = (-144.2 \pm 4.90) + (0.085 \pm 0.002)x$ ,  $n = 3042$ ) than the entire run of data. However, caution in interpreting these trends must be exercised, because the database is composed of multiple individual data sets of greatly varying sampling intensity, each collected by individual labs over particular, often not overlapping, periods of time. Significant differences of up to  $2 \mu\text{M}$  (15% of the mean) in common samples measured by several labs involved in collecting the data in Figure 1 have been reported [*Esterby and Bertram*, 1993]. Unfortunately, the identity of the analyzing lab is a variable strongly aliased with time period in this dataset, and the two cannot be tested simultaneously. Though there is a large sample size, not all points can be considered truly independent, which complicates analysis. Given these considerations, it is still ambiguous whether the lake truly shows any pattern other than a steady, sustained rise, continuing to the present day. Whether  $[\text{NO}_3^-]$  in Lake Superior is leveling in response to policy initiatives cannot be said with great confidence. The data do strongly support a continued rise in lake concentration, in spite of policy-driven leveling of  $\text{NO}_3^-$  emissions. There may

be a long time lag to response for example caused by a slow delivery of past N buildup from the watershed or lake sediments.

[8] In contrast to the unusually good historical record of  $[\text{NO}_3^-]$  in this lake, there is no comparable, reliable record of directly measured phosphate or phosphorus over the same, long time period. However, measurements performed by Environment Canada between 1968 and 2001 show if anything a decline in total phosphorus (TP) and no trend in soluble reactive phosphorus (SRP) (see Figure S1 in auxiliary material) SRP however is at or below the detection limits of standard methods, and has only recently been measured to be on the order of 0.7–4 nM using newer, more sensitive techniques [*Anagnostou and Sherrell*, 2006]. One paleolimnological study, which measured biogenic silica in a single core, offered evidence for a low-level eutrophication of the lake associated primarily with the European settlement in the watershed in the late 1800s [*Schelske et al.*, 2006]. As far as we know, these provocative findings have not yet been corroborated. Though we lack as good a record of phosphorus in the lake as we have for nitrate, there are no data to support an increase in P comparable to the increase in N seen here.

[9] A reference point for  $\text{NO}_3^-:\text{PO}_4^{3-}$  is the Redfield Ratio of 16, which is close to the value observed for the deep ocean and also is an average optimal ratio for ensembles of phytoplankton species [*Klausmeier et al.*, 2004]. The  $\text{NO}_3^-:\text{PO}_4^{3-}$  ratio for Lake Superior today is extremely high, with a vast excess of  $\text{NO}_3^-$  compared to  $\text{PO}_4^{3-}$  relative to the Redfield ratio. Mean deepwater  $[\text{NO}_3^-]$  in the most recent several years is  $26 \mu\text{M}$ , and if we take today's  $[\text{PO}_4^{3-}]$  to be 3 nM, the  $\text{NO}_3^-:\text{PO}_4^{3-}$  ratio would be 8,700, orders of magnitude higher than the Redfield ratio. Given our historical analysis, it is highly likely that the lake is moving steadily further and further away from the Redfield Ratio. To understand the causes of this increasing imbalance, we

**Table 2.** Lake Superior Total N Inputs and Outputs<sup>a</sup>

Source	mmol m <sup>-2</sup> yr <sup>-1</sup>
<i>Inputs</i>	
NH <sub>4</sub> <sup>+</sup> , direct precipitation	12.9
NH <sub>4</sub> <sup>+</sup> tributary input	3.25
Organic N tributary input	22.6
Organic N, direct precipitation	unknown
NO <sub>3</sub> <sup>-</sup> (Table 1)	24.1
Total N input to lake	62.8+
<i>Outputs</i>	
Outflow	
NH <sub>4</sub>	0.18
Dissolved Organic N	4.7
Particulate Organic N	1.05
NO <sub>3</sub> <sup>-</sup> (Table 1)	22.4
Total N output from lake	28.3
N buildup (from Table 1)	23.4

<sup>a</sup>N<sub>2</sub> is not considered. Methods and sources are the same as Table 1. The difference between inputs and the sum of outputs plus buildup (62.8 – (28.3 + 23.4) = 11.1) might be made up by long-term burial or denitrification. N fixation is considered negligible.

can quantify sources and sinks of N in the lake. We therefore constructed annual, lake-wide budgets for NO<sub>3</sub><sup>-</sup> and total N, utilizing the most comprehensive data available (for further details on the construction of the budgets, see the notes in the Table 1). For both, estimates of direct precipitation came from large-scale monitoring projects in U.S. and Canada. For watershed runoff we relied on a somewhat dated, but highly comprehensive unpublished study of the International Joint Commission. Groundwater, a small term, came from a recent, detailed hydrological study plus estimates of groundwater N concentrations. Outflow and buildup terms came from the data in the present study.

[10] Lake Superior lies on the northwestern edge of the well-documented, mid-continental maxima in NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> deposition from agricultural, industrial, and other activities [Galloway *et al.*, 2004; Shannon and Sisterson, 1992]. The NO<sub>3</sub><sup>-</sup> budget of Lake Superior (Table 1) is dominated by three terms: loading from the atmosphere, outflow to the lower Great Lakes, and buildup. However, the inputs and outputs do not balance: combined, the outflow and buildup (45.8 mmol m<sup>-2</sup> yr<sup>-1</sup>) exceed by almost two fold the known external sources of NO<sub>3</sub><sup>-</sup> from the atmosphere and watershed (24.1 mmol m<sup>-2</sup> yr<sup>-1</sup>). This large difference between sources and sinks indicates an in-lake net nitrification rate of 22.1 mmol m<sup>-2</sup> yr<sup>-1</sup>. Though anthropogenically-derived NO<sub>x</sub> deposition may contribute to the long-term trend in [NO<sub>3</sub><sup>-</sup>], the oxidation of reduced forms of N is a very significant part of the N cycle (Tables 1 and 2).

[11] Reduced forms of N to support in-lake nitrification may be ammonium or organic N from tributaries or from direct precipitation (Table 2). These sources (sum = 38.7 mmol m<sup>-2</sup> yr<sup>-1</sup>) are sufficient to support the estimated in-lake nitrification (22.1). Although very few data for in-lake N cycling are available, one study [Heinen and McManus, 2004] estimated NO<sub>3</sub><sup>-</sup> efflux from the sediments to be 26–99 mmol m<sup>-2</sup> yr<sup>-1</sup>. Sedimentary nitrification thus would appear to be a sufficient source of NO<sub>3</sub><sup>-</sup> to account for the estimated in-lake nitrification rate based on Table 1.

[12] In-lake nitrification as the important source of accumulating NO<sub>3</sub><sup>-</sup> is also supported by new observations of stable oxygen isotopes of NO<sub>3</sub><sup>-</sup>, a tracer of atmospheric NO<sub>3</sub><sup>-</sup> [Kendall, 1998]. The δ<sup>18</sup>O<sub>NO3</sub> of the deep water column is 2.47 ± 0.06‰ (SE), which is consistent with in-lake generation of NO<sub>3</sub><sup>-</sup> and 67‰ lower than that of precipitation (69.3 ± 3.8‰). The [NO<sub>3</sub><sup>-</sup>] in Lake Superior is thus driven by active cycling of reduced and oxidized forms of N.

[13] Nitrate in Lake Superior today is far out of stoichiometric balance with PO<sub>4</sub><sup>3-</sup>. It apparently has been rising further and further out of stoichiometric balance for decades. Though it is widely recognized that lakes often exhibit highly imbalanced stoichiometric ratios [Sterner and Elser, 2002], Lake Superior is extreme. Further, the history and mechanism behind this imbalance provide new insights into biogeochemical interactions of N and P.

[14] The [NO<sub>3</sub><sup>-</sup>] buildup likely has several important causes. Although previous studies have pointed to a strong influence of direct deposition of NO<sub>3</sub><sup>-</sup> on the lake surface, our findings strongly suggest that the nitrification of the lake is resulting from in-lake oxidation of reduced forms of N. Biogeochemical mechanisms contributing to the nitrate buildup are as follows. First, owing to its low-P oligotrophic status, the entire lake above the sediment/water interface is an oxidizing environment year-round, favoring transformations of reduced N to nitrate. Biogeochemical processes of ammonium oxidation are increasingly recognized as important components of N cycling. Second, in more productive lacustrine systems, NO<sub>3</sub><sup>-</sup> in the water column can be more thoroughly depleted by biotic uptake and reduced to organic N. Biotic assimilation of NO<sub>3</sub><sup>-</sup> in Lake Superior is greatly constrained by low availability of PO<sub>4</sub><sup>3-</sup>, light and perhaps also iron [Ivanikova *et al.*, 2007; Sterner *et al.*, 2004]. Third, denitrification, which would lower N relative to P, is unlikely to be a major component of the N cycle in the lake. High rates of denitrification require organic C, which is limited due to Lake Superior's low productivity and relatively small watershed compared to lake area. Such factors can have a strong bearing on N cycling in large lakes [Hecky, 2000]. For the above reasons, systems such as Lake Superior that are already strongly constrained other nutrients (i.e. are already stoichiometrically imbalanced) may be most subject to environmental N buildup.

[15] Our work demonstrates that long-term changes in ecosystem N inventory are a result of a complex *in situ* process involving N transformations and possibly time lags, acting in combination with temporal trends in altered input/output of specific forms of N. [NO<sub>3</sub><sup>-</sup>] in Lake Superior is coupled to in-lake source/sink relationships involving input of reduced forms of N, oxidation within the lake, and constrained assimilation and denitrification. Even with long hydraulic residence times and great spatial extent, Redfield N:P balancing mechanisms are not the dominant feature in biogeochemical cycling in this vast, oligotrophic freshwater ecosystem.

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