Isotopic composition of nitrogen in suspended particulate matter of Lake Superior: implications for nutrient cycling and organic matter transformation

**Sanjeev Kumar · Jacques C. Finlay ·
Robert W. Sterner**

Abstract Lake Superior, one of the largest lakes in the world, is an ecosystem where nitrate (NO_3^-) concentration has risen almost fivefold in the last century. Recent studies suggest that this increase may be due to lack of a significant nitrogen (N) sink, such as sedimentary denitrification or burial, because of low organic matter supply to the lake bottom. In light of these new findings, it is imperative to examine the origin and transformation of suspended particulate organic matter (POM) in the lake as N biogeochemistry is inextricably linked to POM dynamics. We present an analysis of spatial and temporal variations in $\delta^{15}N$ of POM ($\delta^{15}N_{POM}$) in the lake and draining rivers based on extensive sampling and a synthesis of recent studies of N cycling. The $\delta^{15}N_{POM}$ in the lake ranged from −4.7 to 7.6‰ and showed a significant ($p < 0.001$) temporal variability in the surface waters with relatively enriched $\delta^{15}N$ during winter (mean ± SD ∼ 1.5 ± 2.3‰; $n = 13$) compared to summer (mean ± SD ∼ −2.0 ± 1.4‰; $n = 20$). Temporal variability in $\delta^{15}N_{POM}$ and data for $\delta^{15}N$ of dissolved inorganic nitrogen (DIN) together suggest a seasonal shift in nutrient sources for plankton along with possible detrital and higher trophic level contributions to POM during winter. On an annual basis, ammonium (NH_4^+) appears to be the dominant N source to plankton in the lake. NO_3^- use was lower but seasonally variable with higher contributions to plankton in summer than winter. During a period of high riverine discharge, no significant difference in coastal and open-lake $\delta^{15}N_{POM}$ was found, indicating limited effect of riverine POM on the lake. Significant increase in $\delta^{15}N_{POM}$ and decreases in particulate N concentration with depth indicate transformations of organic matter settling to the lake bottom that are consistent with the hypothesized influence of low organic matter supply to the lake bottom leading to limited benthic denitrification.

Keywords Lake Superior · Nutrient · Nitrogen · Carbon · Isotope

S. Kumar · J. C. Finlay · R. W. Sterner
Department of Ecology, Evolution, and Behavior, University of Minnesota, 1987 Upper Buford Circle, St. Paul, MN 55108, USA

S. Kumar (✉)
Department of Geography, University of Victoria, Victoria, BC V8W 3R4, Canada
e-mail: kumars@uvic.ca

Introduction

Lake Superior holds almost 10% of Earth's liquid surficial freshwater, making it one of the largest of all lakes. A striking feature of the N cycle of Lake Superior is the conspicuous and unusually steady long-term increase in NO_3^- concentration, which has increased almost fivefold (∼5–25 μM) since the early 1900s to the present (Bennett 1986; Sterner

et al. 2007). Earlier studies attributed this increase to atmospheric deposition of NO_x emissions (Bennett 1986; Ostrom et al. 1998). However, recent studies based on a whole-lake N budget, planktonic N uptake, and N and oxygen (O) stable isotopes in NO_3^- of the lake water and precipitation suggest internal N cycling to be the principal source of NO_3^- in the lake's waters (Sterner et al. 2007; Finlay et al. 2007; Kumar et al. 2008). The construction of whole-lake NO_3^- and N budgets of the lake revealed that NO_3^- must be generated in the lake at significant rates (Sterner et al. 2007). Stable isotope results also indicated that most NO_3^- in the lake originated by in-lake oxidation (Finlay et al. 2007). Therefore, NO_3^- in Lake Superior responds not just to NO_3^- loading but also to oxidation of reduced forms of N delivered to the lake (Sterner et al. 2007).

In light of this new view on one of the most important biogeochemical aspects of the lake, better understanding of the origin and transformation of suspended particulate organic matter (POM) is necessary to better comprehend the sources and sinks of N in the lake. Lake Superior is oligotrophic with water-column production rates $\sim$150–350 mg C m^{-2} day^{-1} (Sterner 2010) and by virtue of its depth organic carbon may be extensively mineralized before settling into sediments. Thus, Lake Superior may lack an effective NO_3^- sink, like sedimentary denitrification or burial, due to the low organic matter supply to the lake's bottom (Carlton et al. 1989; Baker et al. 1991; Kumar et al. 2008). Low productivity along with remineralization during settling may lead to an insufficient supply of organic matter to the lake bottom to drive an extensive NO_3^- removal through denitrification or sedimentary burial. At present, however, there are little data to directly address this hypothesis (Carlton et al. 1989; Baker et al. 1991).

The stable isotopic composition of N in POM ($\delta^{15}N_{POM}$) could provide insights into the origin and transformations of POM, which would enable us to understand nutrient utilization and fate of organic matter in the lake. The $\delta^{15}N$ of organic and inorganic pools of aquatic systems varies significantly over a range of spatial and temporal scales (e.g., Altabet 1996; Rau et al. 1998; Ostrom et al. 1998; Keough et al. 1996; Harvey and Kitchell 2000; Kendall et al. 2001; Cloern et al. 2002). Isotopic variations in different chemical species of N are caused by mass

dependent fractionations associated with various biogeochemical transformations such as denitrification, nitrification, NO_3^- assimilation, and N_2 fixation (Mino et al. 2002). Nitrification and denitrification cause progressive isotopic enrichment of the remaining NH_4^+ and NO_3^- pool, respectively, whereas the large isotopic fractionation associated with nitrification leads to depleted $\delta^{15}N$ in NO_3^- ($\delta^{15}N_{NO_3^-}$; Liu et al. 1989; Pennock et al. 1996). Assimilation of NO_3^- and NH_4^+ by plankton also causes enrichment in ^{15}N of the remaining dissolved inorganic nitrogen (DIN) pool (McCusker et al. 1999). Fixation of N_2 lowers $\delta^{15}N_{POM}$ (<0‰) compared to that typically formed utilizing NO_3^- and NH_4^+ (1.3–7.6‰; Rau et al. 1998) as atmospheric N has $\delta^{15}N = 0‰$.

In aquatic systems, where phytoplankton are a significant component of seston, as is the case in Lake Superior (Halfon 1984; Cotner et al. 2004), the isotopic composition of POM is largely governed by isotopic fractionation during uptake by phytoplankton and the isotopic composition of source nutrients (McCusker et al. 1999). Generally, the relationship between POM isotopic composition, substrate isotopic composition, and substrate concentration can be modelled with Rayleigh fractionation kinetics for closed systems. Based on these kinetics, the isotopic composition of POM is enriched as the isotopic composition of substrate gets heavier due to its progressive use, i.e., decrease in its concentration. Using this relationship, $\delta^{15}N_{POM}$ can be an index of nutrient availability and utilization (Altabet 1996). For example, where only one form of N (e.g., NO_3^-) is a primary source, there will be a negative correlation between $\delta^{15}N_{POM}$ and nutrient concentration (Altabet and McCarthy 1986). However, $\delta^{15}N_{POM}$ does not remain a reliable index of nutrient utilization when different nutrient sources (e.g., NO_3^-, NH_4^+, and dissolved organic N) with distinct isotopic signatures are used by phytoplankton (Montoya et al. 1991; Carpenter et al. 1997; Rau et al. 1998).

The $\delta^{15}N_{POM}$ in Lake Superior has been measured previously (Pang and Nriagu 1977; Keough et al. 1996; Ostrom et al. 1998; Harvey and Kitchell 2000; Sierszen et al. 2006) and it ranges from −2 to 6.9‰, similar to the typical $\delta^{15}N$ (from −5.7 to 10.6‰) for freshwater seston (Cloern et al. 2002). Most of the earlier studies emphasized local food web dynamics (Keough et al. 1996; Harvey and Kitchell 2000), had

limited sample sizes, or narrow geographic and temporal extent (Pang and Nriagu 1977; Ostrom et al. 1998). There is also a limited knowledge of depth-dependent variation in $\delta^{15}N_{POM}$ (Ostrom et al. 1998; Sierszen et al. 2006) in the lake, which is known to increase with depth in marine systems (e.g., Saino and Hattori 1980; Altabet 1996; Minagawa et al. 2001). Our study presents comprehensive temporal, spatial, and depth-dependent measurements of $\delta^{15}N_{POM}$ in Lake Superior and reports the first ever values, to the best of our knowledge, of $\delta^{15}N_{POM}$ during winter along with an evidence of depth-dependent increase in $\delta^{15}N_{POM}$. We also present the preliminary result of $\delta^{15}N$ of NH_4^+ $\left(\delta^{15}N_{NH_4^+}\right)$ in the lake water.

The main aim of this study was to examine the origin and transformation of POM in Lake Superior in light of recent studies that indicate dominance of internal N cycling and low rates of N removal in the lake sediments. Our study focused on exploring the biogeochemical characteristics of an oligotrophic lake where organic matter dynamics plays a key role in determining the fate of N and which exhibit long-term N accumulation. The specific goals of the study were to (i) investigate spatial and temporal variation in $\delta^{15}N_{POM}$ in the lake and several tributary rivers, (ii) evaluate the relative role of NO_3^- and NH_4^+ in origin of POM in the lake using $\delta^{15}N_{POM}$, published $\delta^{15}N_{NO_3^-}$, and new $\delta^{15}N_{NH_4^+}$ data, (iii) investigate

possible seasonal shifts in nutrient sources (NO_3^- or NH_4^+) for plankton, and (iv) explore depth-dependent transformation of POM.

Materials and methods

This study is a part of a larger project focussed on understanding the N and carbon (C) biogeochemistry of Lake Superior (Sterner et al. 2007; Kumar et al. 2007; Finlay et al. 2007; Kumar et al. 2008; Sterner 2010). Ambient NO_3^- (Sterner et al. 2007), NH_4^+ (Kumar et al. 2007), and $\delta^{15}N_{NO_3^-}$ (Finlay et al. 2007) were measured as part of the project, and data from these previous studies are used in analyses of $\delta^{15}N_{POM}$ data from the present study.

Samples were collected during several different cruises onboard the R/V Blue Heron and the R/V Limnos during 2005–2007 at locations distributed widely across the lake (Fig. 1; Table 1). Twelve major and minor rivers draining into Lake Superior were also sampled during May 2005 (Table 2), a period of high water discharge (http://waterdata.usgs.gov/nwis/monthly).

Water samples were collected from different depths using Niskin bottles attached to a CTD rosette. Duplicate samples of up to 2 l of lake water were filtered using precombusted (4 h @ 450°C) 25 mm Whatman GF/F filters except during May and July

Fig. 1 Sampling locations and some of the major rivers draining into Lake Superior
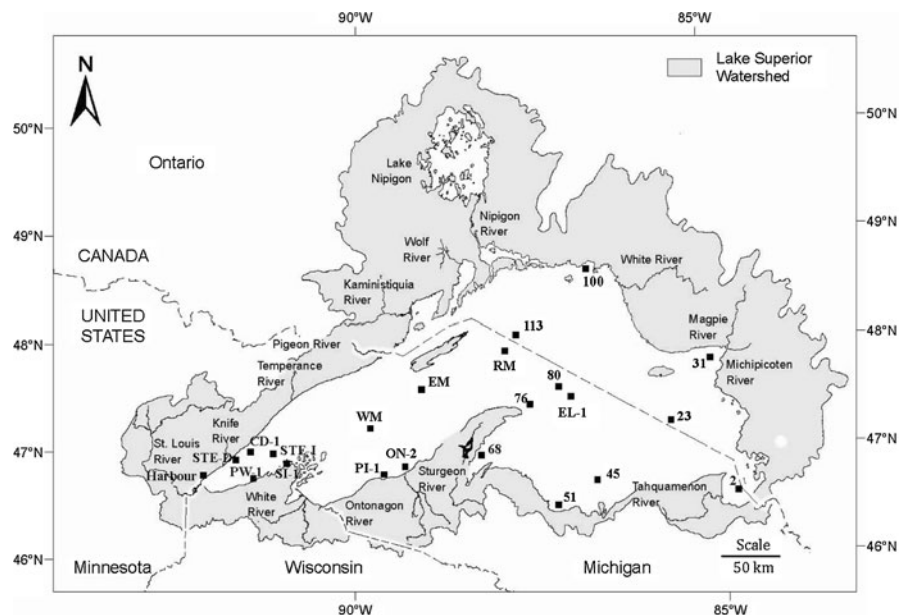
Table 1 Sampling locations

Cruises	Period	Stations covered
LIMNOS	24 May to 31 May 2005	2, 23, 31, 45, 51, 68, 76, 100, 113
NILS 4	6 June to 9 June 2005	CD-1, STE-I, ON-2, PW-1, PI-1, CH-1, Harbour
NILS 5	20 July to 22 July 2005	CD-1, WM, RM, EM
NILS 6	28 Aug to 1 Sep 2005	ON-2, EL-1, PW-1
NILS 7	17 Sep 2005	CD-1
NILS 8	2 Oct 2005	CD-1
LIMNOS	7 Oct 2005	113
NILS 9	31 Jan 2006	CD-1, STE-D
NILS 10	22 Mar 2006	CD-1
NILS 12	20 Jun 2006	CD-1
NILS 13	11 July to 14 July 2006	CD-1, EL-1, RM
NILS 14	8 Aug to 11 Aug 2006	CD-1, SI-1, EM
NILS	1 Jun 2007	G
CARGO 2	5 Oct 2007	CD-1
Rivers	24 May to 26 May 2005	St. Louise, Knife, Nemadji, Lester, Kamantiqua, Chester, Kingsbury, Temperance, Wolf, Hollow, Tischer, Pine

Table 2 Particulate organic nitrogen concentration along with isotopic composition in major and minor rivers draining into Lake Superior

Sampling date	Rivers	PON (μM N)	NO_3^- (μM)	$\delta^{15}N_{POM}$ (‰)
24 May 2005	St. Louis	0.9	5.7	2.5
25 May 2005	Knife	2.1	1.1	2.7
27 May 2005	Nemadji	14.4	4.6	1.9
25 May 2005	Lester	2.4	0.5	1.1
26 May 2005	Kamantiqua	2.6	2.6	2.1
24 May 2005	Chester	2.0	1.1	3.8
24 May 2005	Kingsbury	1.7	1.9	2.9
25 May 2005	Temperance	2.0	3.3	2.4
26 May 2005	Wolf	1.3	5.0	2.0
26 May 2005	Hollow	3.4	3.5	2.6
24 May 2005	Tischer	2.9	2.2	2.8
26 May 2005	Pine	2.8	5.0	3.0

2005 when only a single sample was collected at each station. Only up to 500 ml of water was filtered for river samples due to clogging of filters. Samples were frozen immediately after filtration and were later dried for analysis. Isotopic composition of N along with particulate N content was analyzed in the same sample using a stable isotope ratio mass spectrometer coupled to an elemental analyzer. The isotopic analysis was performed at stable isotope facilities at the University of California, Davis and the Northern Arizona University with analytical precision of ±0.3‰.

Results are expressed in δ values, as the per mil (‰) deviation from the atmospheric N_2 standard, where:

$$\delta^{15}N = \left[\left(R_{sample} - R_{standard} \right) / R_{standard} \right] \times 1000,$$
$$R = {}^{15}N/{}^{14}N.$$

The $\delta^{15}N_{NH_4^+}$ in Lake Superior was measured at a single site in July 2006 using the NH_4^+ diffusion method adapted for low NH_4^+ concentrations (Holmes et al. 1998). Water from 25 m depth at CD-1 (NH_4^+ concentration $\sim$ 0.20 μM) was filtered

(GF/F) and similar volumes (4 l) of lake and ultrapure water were transferred to duplicate 8 l high-density polyethylene diffusion bottles. Ammonium sulfate with a known $\delta^{15}N$ value (0.4‰) was added to the ultrapure bottle in amounts equivalent to ambient NH_4^+ concentration in the lake to provide a standard. After adding NaCl, filter packs prepared using GF/D filter paper (containing 25 μl of 2 M H_2SO_4) and Teflon were introduced into diffusion bottles. These bottles were closed tightly immediately after adding MgO. The whole bottle set was shaken for 14 days. After 14 days of diffusion, the filter packs were dried under concentrated H_2SO_4 and were subsequently analyzed for $\delta^{15}N$. $\delta^{15}N_{NH_4^+}$ was obtained by correcting $\delta^{15}N$ of filter papers in sample diffusion bottles (-19.3 ± 0.1‰) using $\delta^{15}N$ of filter papers in standard diffusion bottles (-21.6 ± 0.05‰). The method applied for correction and error analysis was similar to Holmes et al. (1998).

Results

Temperature

Lake Superior is cold and deeply mixed most of the year. During the present study, the lake was deeply mixed from January to May with water column temperature around 3.5°C (Fig. 2). During June, the lake started to show shallow summer stratification on the southern margin (sites ON-2 and STE-I during 2005) while remaining deeply mixed at others (PI-1

and CD-1). Stratification was lake-wide during July and August with surface temperature varying between 11.6°C at site RM (July 2005) to 20.7°C at CD-1 (August 2006). In general, the thermocline was around 20–40 m during July and August. The lake was also stratified during September and October at CD-1 (only station covered) with surface temperature around 13.5°C. Typical temperature profiles observed seasonally at CD-1 are shown in Fig. 2. In the following sections, for the interpretation purpose, months covered during the study period have been categorized into deeply mixed (January–May; henceforth "winter") and shallow stratified (June–October; henceforth "summer") periods.

$\delta^{15}N_{POM}$ and PON concentration in the lake

$\delta^{15}N_{POM}$ in Lake Superior varied from -4.7‰ at mid-lake station EL-1 (20 m) during August 2005 to a maximum of 7.6‰ in surface waters of nearshore station STE-D during January 2006. The average $\delta^{15}N_{POM}$ calculated by averaging all data was 0.2 ± 2.6‰ (mean $\pm$ SD; $n = 101$). The average value reported here is within the range of values reported earlier but the range we observed was much wider than for previous studies (Table 3). The average particulate organic nitrogen (PON) concentration was 0.9 ± 0.4 μM N (mean $\pm$ SD; $n = 101$).

Variation by time and depth

The surface (top 5 m) $\delta^{15}N_{POM}$ in Lake Superior was significantly enriched ($p < 0.001$; ANOVA) during winter compared to summer (Fig. 3). The lake-wide average $\delta^{15}N_{POM}$ in surface waters during winter
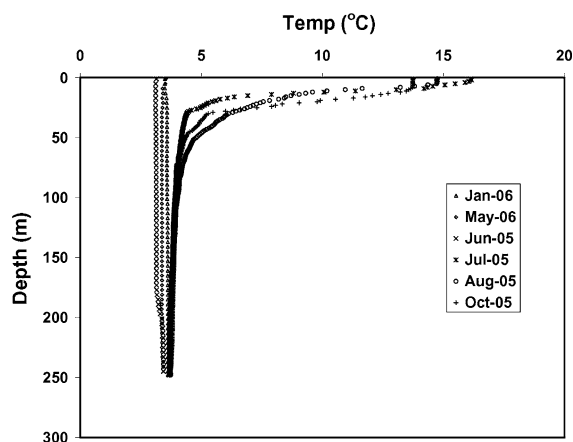
Fig. 2 Typical temperature profiles observed at CD-1

Table 3 Comparison of nitrogen isotopic composition in suspended particulate organic matter of Lake Superior from different studies

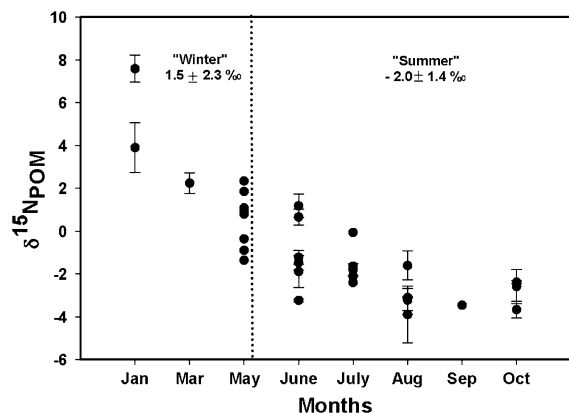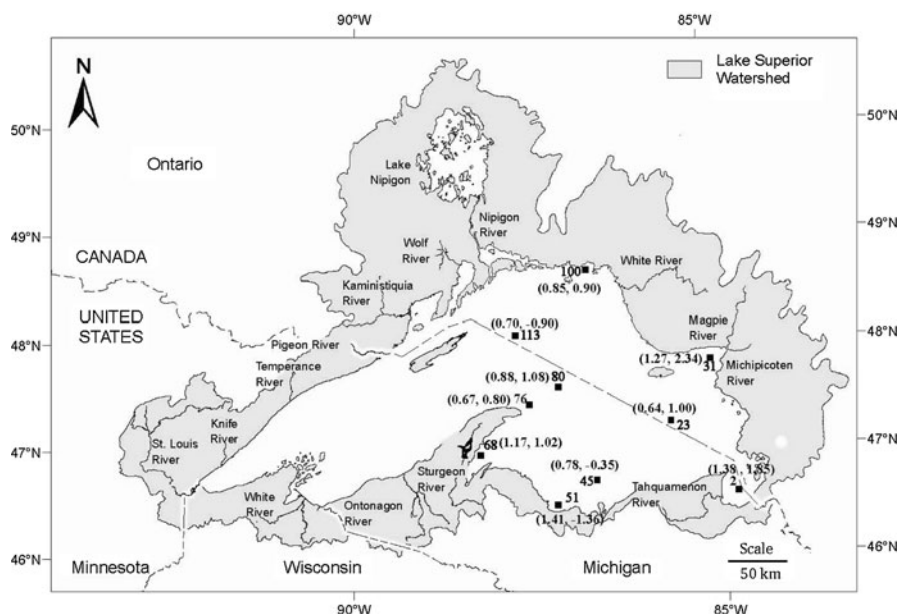| References	$\delta^{15}N_{POM}$ (‰)
Pang and Nriagu (1977)	1.6
Keough et al. (1996)	1.6 to 2.1 (53–163 μm)
Keough et al. (1996)	-0.6 to -0.2 (<53 μm)
Harvey and Kitchell (2000)	0.35 to 3.88
Ostrom et al. (1998)	0 to 7
Sierszen et al. (2006)	-1.8 to 4.5
This study	-4.7 to 7.6

Fig. 3 Month-wise variation in surface (top 5 m) $\delta^{15}N_{POM}$ (‰) during the study period. Error bars represent 1 SD for duplicate samples. Numeric values within the graph are mean ± SD of surface $\delta^{15}N_{POM}$ during "winter" and "summer" approximately separated by the dotted line

months was 1.5 ± 2.3‰ (mean ± SD; $n = 13$) compared to -2.0 ± 1.4‰ (mean ± SD; $n = 20$) during summer months. At a majority of sites during winter months, $\delta^{15}N_{POM}$ in surface waters was greater than 0‰ (Figs. 3, 4), whereas during summer months it was less than 0‰ at most of the sites (Figs. 3, 5). The average $\delta^{15}N_{POM}$ in surface water during August (mean ± SD $\sim -3.0 \pm 0.8$‰; Fig. 5) and September (CD-1 ~ -3.4‰; Fig. 6) were among the lowest observed in the lake.

In order to assess the possible physical and biogeochemical causes of temporal variation, we focused on CD-1, the most thoroughly sampled station during the study, which was located in the south-western portion of the lake (Fig. 6). Data from this station indicate enriched $\delta^{15}N_{POM}$ in surface during winter (January $\sim 3.9 \pm 1.1$‰; March $\sim 2.3 \pm 0.5$‰; mean ± SD; $n = 2$) compared to other months (no sample was collected during May at this station), when $\delta^{15}N_{POM}$ was less than -1.8‰ (Fig. 6a). The highest $\delta^{15}N_{POM}$ during the study period (mean ± SD $\sim 7.6 \pm 0.6$‰; $n = 2$) was also observed in the surface water at a nearby site (STE-D) during January (Fig. 6). No reliable data from deeper depths during January and March could be obtained due to the very low N concentration of the material collected on filters. PON concentration in the surface water was lowest during January (Fig. 6b).

In general, $\delta^{15}N_{POM}$ increased and PON decreased with depth (Figs. 5, 6). Average $\delta^{15}N_{POM}$ for the study period in the top 25 m of the water column at CD-1 was -1.6 ± 2.0‰ (mean ± SD; $n = 16$) which increased to 3.5 ± 2.2‰ (mean ± SD; $n = 4$) near the lake bottom (~ 250 m). The PON concentration at CD-1 averaged around 1.1 ± 0.4 µM N (mean ± SD) in the top 25 m and decreased to 0.5 ± 0.1 µM N (mean ± SD) near the bottom (Fig. 6).
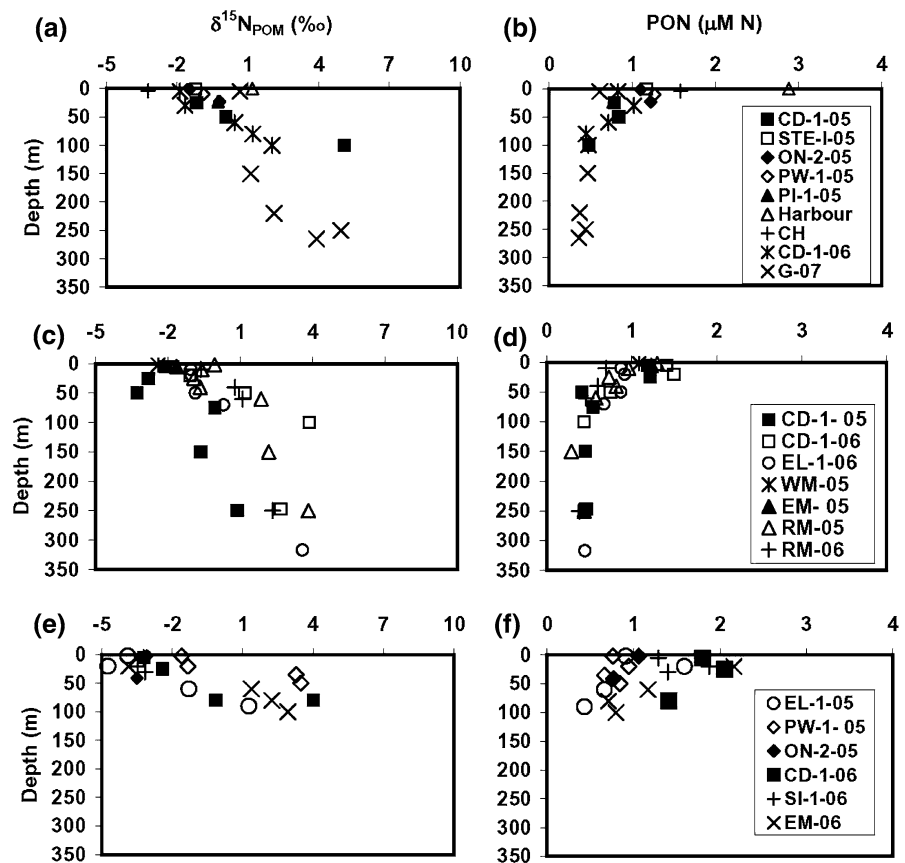
Fig. 4 Suspended particulate organic nitrogen concentration (first in parentheses) and nitrogen isotopic composition (second in parentheses) in surface waters during May 2005

Fig. 5 Vertical profiles of $\delta^{15}N_{POM}$ and PON during June (**a**, **b**), July (**c**, **d**), and August (**e**, **f**) at different stations. Both $\delta^{15}N_{POM}$ and PON have same symbols for a particular month

Spatial variation

Only surface water was sampled during May 2005 to examine spatial patterns in $\delta^{15}N_{POM}$ during period of high river discharge. It varied from −1.4‰ at stn 51 to 2.3‰ at stn 31 with an overall average of 0.6 ± 1.2‰ (mean $\pm$ SD; $n = 10$; Fig. 4). There was no significant difference in $\delta^{15}N_{POM}$ ($p > 0.05$; ANOVA) values for coastal (~25 km; mean $\pm$ SD ~ 0.9 ± 1.3‰; $n = 6$) and open (mean $\pm$ SD ~ 0.2 ± 0.9‰; $n = 4$) lake stations.

Analysis of spatial variation in all surface samples during the study period (data shown in Fig. 3) also indicated higher average $\delta^{15}N_{POM}$ (mean $\pm$ SD ~ -0.3 ± 2.9‰; $n = 20$) and PON (1.2 ± 0.5 μM N; $n = 20$) at stations closer to the coast compared to open-lake stations (mean $\pm$ SD ~ -0.7 ± 1.7‰; 0.9 ± 0.2 μM N, respectively; $n = 9$). However, this difference was also not statistically significant (ANOVA; $p > 0.05$ for both $\delta^{15}N_{POM}$ and PON).

Relationships among nutrients concentration and $\delta^{15}N_{POM}$

In order to examine the relative role of NO_3^- and NH_4^+ in formation of POM, relationships among data for surface $\delta^{15}N_{POM}$, NO_3^- (from Sterner et al. 2007) and NH_4^+ (from Kumar et al. 2007) concentrations in the lake and rivers were examined. A weak positive relationship ($R^2 = 0.20$; $p = 0.01$) between $\delta^{15}N_{POM}$ and NO_3^- (Fig. 7a) was observed, in contrast to a strong negative relationship ($R^2 = 0.45$; $p = 0.0003$) between $\delta^{15}N_{POM}$ and NH_4^+ (Fig. 7b). In other words, when NO_3^- concentration was low in surface waters, usually during summer due to NO_3^- uptake (drawdown of ~1.3 μM from June to August; Kumar et al. 2008), $\delta^{15}N_{POM}$ was depleted, suggesting use of ^{15}N depleted NO_3^- (Finlay et al. 2007). When NH_4^+ concentration was low in surface water (~0.12 μM during winter compared to >0.2 μM during summer at most stations; Kumar et al. 2007),

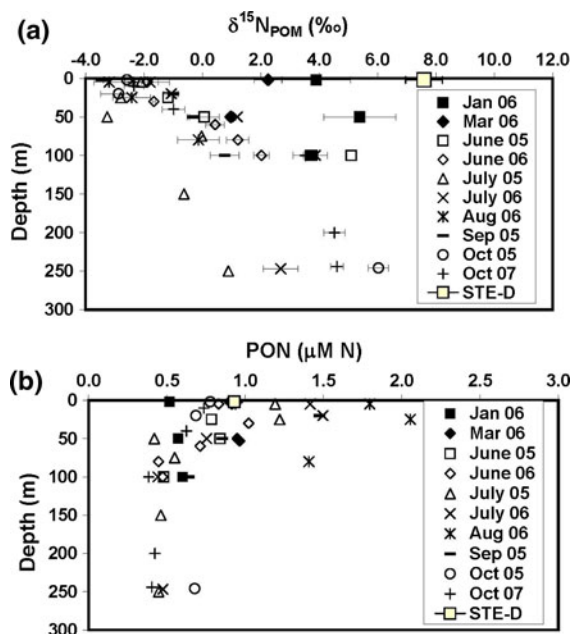**Fig. 6** Vertical profiles of **a** $\delta^{15}N_{POM}$ and **b** PON at CD-1 during different months. Value at STE-D during January 2006 is also shown. A typical variation observed in $\delta^{15}N_{POM}$ for duplicate samples are shown as error bars (1 SD), except during July 2005 where single sample was collected at each depth. The variations in PON were less than 10% for majority of samples and were less than symbol thickness
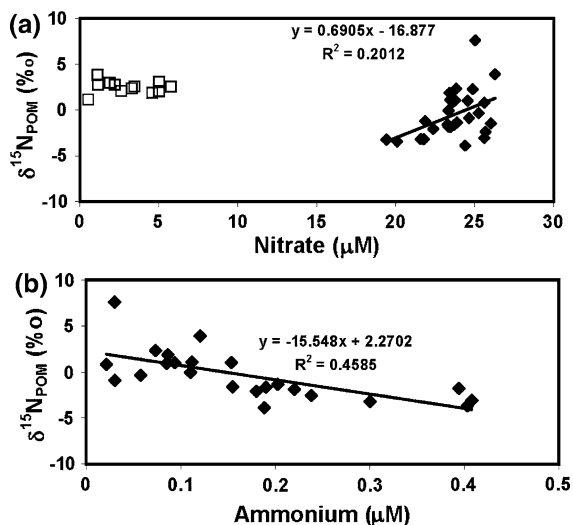

Fig. 7 Relationships between **a** $\delta^{15}N_{POM}$-NO_3^- and **b** $\delta^{15}N_{POM}$-NH_4^+ for the lake surface (*dark symbols*) and rivers (*open symbol*)

$\delta^{15}N_{POM}$ was enriched, consistent with use of ^{15}N enriched NH_4^+ (see "Isotopic composition of NH_4^+ in the lake" section). These relationships indicate the

importance of both NO_3^- and NH_4^+ in formation of POM.

Isotopic composition of organic matter in rivers

The river sampling was performed to assess the effect of riverine discharge on coastal POM of the lake. The samples were collected during May, therefore data presented here represent a single survey of rivers during springtime high runoff conditions. The average $\delta^{15}N_{POM}$ (mean ± SD ∼ 2.5 ± 0.7‰; $n = 12$) and PON concentration (mean ± SD ∼ 3.2 ± 3.6 μM N; $n = 12$) of rivers draining into Lake Superior (Table 2) were higher than the average $\delta^{15}N_{POM}$ and PON concentration in the lake. Unlike the lake, no relationship between $\delta^{15}N_{POM}$ and NO_3^- was observed (Fig. 7a). We do not have NH_4^+ concentrations for river samples.

Isotopic composition of NH_4^+ in the lake

We are not aware of any published data for $\delta^{15}N_{NH_4^+}$ in Lake Superior. Determination of precise $\delta^{15}N_{NH_4^+}$ in the lake is difficult due to very low NH_4^+ concentration. Our measurements at 25 m at CD-1 on a single date (July 2006; 0.20 μM) showed $\delta^{15}N_{NH_4^+}$ at 2.7 ± 0.1‰ ($n = 2$).

Discussion

A century-long steady increase in NO_3^- concentration of Lake Superior represents an unusually extensive record of N buildup in an ecosystem (Sterner et al. 2007). Previous studies based on direct N uptake (Kumar et al. 2008) and denitrification (Carlton et al. 1989) rates measurements suggest that while N is actively cycling in the lake, there is not an effective sink for N removal through denitrification. The apparent lack of N removal may be linked to limited organic matter supply to the lake bottom as well as active N recycling in the oxic water column (Sterner et al. 2007; Finlay et al. 2007; Kumar et al. 2008). Given the inextricable link between organic and inorganic pools of N, it is important to understand the origin and transformation of POM in the lake, particularly the role of different nutrients and depth-dependent transformations. The stable isotope data presented here indicate temporal variation in

$\delta^{15}N_{POM}$ with relatively enriched surface $\delta^{15}N_{POM}$ during winter compared to summer along with depth-dependent enrichment in $\delta^{15}N_{POM}$. There are several possible mechanisms that could produce observed temporal variability in surface $\delta^{15}N_{POM}$, such as: (i) temporal shift in nutrient use (NO_3^- and NH_4^+) by phytoplankton and bacteria, (ii) mixing of ^{15}N enriched deeper particulate matter with surface POM during winter, (iii) inclusion of higher trophic levels or detrital material in POM samples during winter, and (iv) N_2-fixation during summer. Below, we explore the above-mentioned possibilities and implications of the observed results on N biogeochemistry of the lake.

POM formation and role of nutrients

Lake Superior is an oligotrophic lake with high NO_3^- concentration (~ 25 μM) and extremely low availability of phosphorus (Sterner et al. 2007). Given the large NO_3^- pool, it was previously thought that NO_3^- was the primary source of inorganic N for phytoplankton in the lake (Ostrom et al. 1998). However, a ^{15}N based tracer study for the summer (June–August) revealed that despite being almost 125 times lower than NO_3^-, NH_4^+ contributes $\sim 75\%$ of the total N ($NO_3^- + NH_4^+$) uptake by plankton in the lake (Kumar et al. 2008). No direct measurements of the relative contribution of NO_3^- and NH_4^+ to the total N uptake during winter are available, but variations in $\delta^{15}N_{POM}$ can be used to infer the role of DIN species (NO_3^- and NH_4^+) to N uptake as $\delta^{15}N_{POM}$ is primarily related to $\delta^{15}N$ of DIN ($\delta^{15}N_{DIN}$) and isotopic fractionation (ε) associated with DIN uptake by plankton. Unlike relatively smaller and eutrophic lakes where $\delta^{15}N_{DIN}$ and $\delta^{15}N_{POM}$ often vary by more than 15‰ over an annual cycle (e.g., Lehmann et al. 2004; Hadas et al. 2009; Gu 2009), $\delta^{15}N_{POM}$ (from −4.7 to 7.6‰; present study) and $\delta^{15}N_{DIN}$ ($\delta^{15}N_{NO_3^-}$: from −2.5 to −1.6‰; Finlay et al. 2007) in Lake Superior showed a relatively restricted range. The temporal variation in surface $\delta^{15}N_{POM}$ of Lake Superior does suggest, however, important seasonal shifts in nutrient sources by plankton.

In aquatic systems, variations in $\delta^{15}N_{POM}$ have often been attributed to the isotopic effect associated with NO_3^- uptake where phytoplankton preferentially incorporate the lighter isotope (e.g., Altabet et al. 1991; Holmes et al. 1999; Fogel and Cifuentes 1993). Therefore, if NO_3^- uptake is the major control on $\delta^{15}N_{POM}$, $\delta^{15}N_{POM}$ should be less than or equal to that of $\delta^{15}N_{NO_3^-}$. A wide range of $\delta^{15}N_{POM}$ values were observed during the present study (mean ± SD $\sim -0.6 \pm 2.5$‰ in surface water), many of which were greater than $\delta^{15}N_{NO_3^-}$. This suggests that NO_3^- uptake is not the only control on $\delta^{15}N_{POM}$. The variability in $\delta^{15}N_{POM}$ probably reflects the variable contributions of NO_3^- and NH_4^+ during different periods.

One of the reasons for lower average $\delta^{15}N_{POM}$ during summer compared to winter appears to be relatively higher uptake of NO_3^- during summer than winter. Although limited to a single data point, $\delta^{15}N_{NH_4^+}$ (2.7‰) in the lake during the present study is enriched compared to overall $\delta^{15}N_{NO_3^-}$ (mean ± SD $\sim -2.3 \pm 0.3$‰; $n = 34$; Finlay et al. 2007), a commonly observed feature in freshwater systems because of the large fractionation associated with nitrification (Liu et al. 1989; Pennock et al. 1996). Despite the overall depleted $\delta^{15}N_{NO_3^-}$, the average $\delta^{15}N_{NO_3^-}$ in the surface during summer (mean ± SD $\sim -1.7 \pm 0.03$‰; $n = 6$; Finlay et al. 2007) was enriched compared to winter (March = −2.4‰; Finlay et al. 2007) indicating higher NO_3^- uptake during summer than winter. Deep water NO_3^- was not ^{15}N-enriched, so that the observed enrichment in surface $\delta^{15}N_{NO_3^-}$ during summer appears to be entirely due to biological uptake of NO_3^- because discrimination against ^{15}N during uptake leaves the remaining NO_3^- pool ^{15}N-enriched (Fig. 8). This higher uptake of a ^{15}N depleted source (NO_3^-) during summer compared to winter likely led to depleted surface $\delta^{15}N_{POM}$ during summer. This is also supported by a significant positive relationship between surface $\delta^{15}N_{POM}$ and NO_3^- (Fig. 7a) suggesting depleted $\delta^{15}N_{POM}$ during period of lower NO_3^- (i.e., during summer), possibly due to NO_3^- uptake. On the other hand, $\delta^{15}N_{POM}$ was enriched when NH_4^+ was lower in surface waters, during winter, suggesting that greater use of ^{15}N enriched NH_4^+ may account for enriched $\delta^{15}N_{POM}$ during winter.

Further analyses of the relative role of NO_3^- versus NH_4^+ can be illustrated by employing Rayleigh fractionation kinetics. The removal of NO_3^- due to biological uptake by plankton leads to enrichment in the remaining pool and is expressed by Rayleigh fractionation as:

$$\delta^{15}N_{NO_3^-} = \delta^{15}N_{NO_3^- \ (f=1)} - \varepsilon_{NO_3} \times \ln f \qquad (1)$$

where, f is the fraction of NO_3^- remaining and ε_{NO_3} is the fractionation factor for NO_3^- uptake in ‰. The application of this relationship to typical vertical profiles of $\delta^{15}N_{NO_3^-}$ and NO_3^- concentration during late summer (September 2005) at CD-1 (Fig. 8) yields a ε_{NO_3} (slope $= -1 \times \varepsilon$) of 2.4‰ (Fig. 9). This estimation ($\varepsilon_{NO_3} = 2.4$‰) is based on an assumption that each point in the vertical profile during September had the same initial $\delta^{15}N_{NO_3^-}$ and NO_3^- concentration before removal of NO_3^- due to biological uptake (Altabet 1996). This assumption appears to be reasonable as deeper waters during September have almost similar values as January (assuming January to be initial; Fig. 8). Based on the
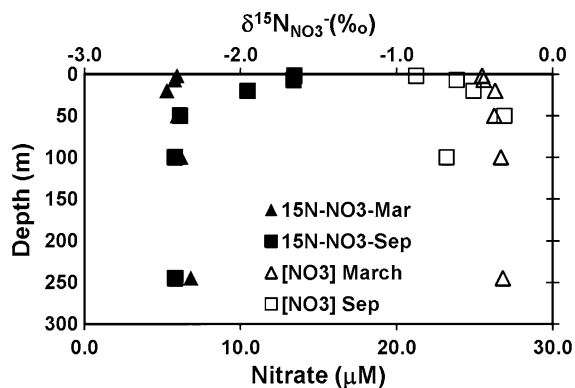

Fig. 8 Typical depth profiles of NO_3^- concentration and $\delta^{15}N_{NO_3^-}$ during winter (March 2006) and late summer (September 2005) at CD-1. $\delta^{15}N_{NO_3^-}$ data from Finlay et al. (2007)

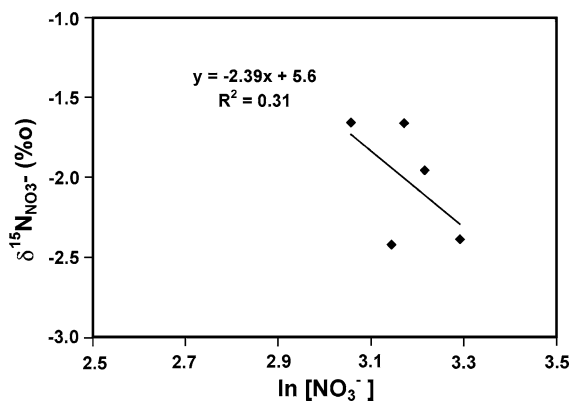**Fig. 9** Relationship between $\delta^{15}N_{NO_3^-}$ and ln $[NO_3^-]$ for the depth profile at CD-1 shown in Fig. 8 during September 2005

same fractionation kinetics, assuming NO_3^- as the only source of N for phytoplankton, the $\delta^{15}N_{POM}$ at any point of time is given as:

$$\delta^{15}N_{POM} = \delta^{15}N_{NO_3^-} - \varepsilon_{NO_3}. \qquad (2)$$

Since the typical $\delta^{15}N_{NO_3^-}$ in the surface water during summer is around -1.70 ± 0.03‰ (mean $\pm$ SD), the expected $\delta^{15}N_{POM}$ formed entirely with NO_3^- should be around -4.1‰. This expected $\delta^{15}N_{POM}$ is closer to the observed surface $\delta^{15}N_{POM}$ during summer than winter, suggesting relatively higher NO_3^- signature during summer compared to winter. Nevertheless, most of the surface $\delta^{15}N_{POM}$ during summer (mean $\pm$ SD $\sim -2.0 \pm 1.4$‰) were higher than -4.1‰, which indicates contributions from enriched nutrient sources (i.e., NH_4^+) to the plankton as well. The limited data for $\delta^{15}N_{NH_4^+}$ in the lake, however, restricts us to quantify the contributions of NO_3^- and NH_4^+ to plankton more definitively using this technique.

While we have argued that the seasonal variation in $\delta^{15}N_{POM}$ is directly related to seasonal shifts in N use by phytoplankton, there are several alternative explanations to be considered. First, the enrichment in surface $\delta^{15}N_{POM}$ during winter may also be caused by mixing of ^{15}N enriched POM from deeper layers due to winter mixing. However, an equal proportion mixing of deeper (6.03‰) and surface (-2.58‰) POM at CD-1 during October 2005, the last month before winter for which data are available, resulted in $\delta^{15}N_{POM}$ of 1.70‰, considerably lower than the observed surface value during January 2006 at CD-1(~ 3.9‰). Second, higher $\delta^{15}N_{POM}$ during winter could also be due to greater inclusion of higher trophic levels or detritus materials in POM samples during winter compared to summer. Destratification may augment the refractory contribution to POM by preventing the maintenance of phytoplankton within euphotic zone and favoring resuspension of sediment organic matter (Ostrom et al. 1998). Higher microzooplankton grazing during winter could also result in higher $\delta^{15}N_{POM}$ as this has been shown to be responsible for enrichment in $\delta^{15}N_{POM}$ by 3–5‰ (Hoch et al. 1996). We do not have data to address these hypotheses and these must remain untested at the present time. Finally, seasonal patterns of $\delta^{15}N_{POM}$, particularly depleted surface $\delta^{15}N_{POM}$ during summer, could be related to N_2-fixation.

While it is not possible to distinguish N_2-fixation from other processes with natural abundance ^{15}N in Lake Superior because of overlapping signatures, an earlier study suggests that N_2-fixation is of little importance in the lake, consistent with the phosphorus poor but N rich nature of the lake (Mague and Burris 1973). Although N_2-fixation in lakes with high DIN has been reported, its contribution to total fixed N remain smaller (2–9%) compared to DIN uptake (Ferber et al. 2004; McCarthy et al. 2007).

Assuming the above mentioned contributors (detritus, higher trophic level and N_2-fixation) to be not significant, it appears from the present study and a tracer based N uptake study (Kumar et al. 2008) that on an annual basis NH_4^+ remains the dominant nutrient source for phytoplankton and bacteria in Lake Superior with variable contributions from NO_3^-. The contribution of NO_3^- is relatively higher during summer than winter. During winter, when total N uptake is lower compared to summer due to lower temperature (Kumar et al. 2008), the N uptake in the lake appears to be dominated by NH_4^+. This is consistent with other lake-based studies which found NH_4^+ to be dominant N source on annual basis (Axler et al. 1981; Berman et al. 1984; Fisher et al. 1988; Ferber et al. 2004) with occasional spring or autumn use of NO_3^- (Berman et al. 1984; Takahashi and Saijo 1988). Higher $\delta^{15}N_{POM}$ during spring compared to summer due to utilization of ^{15}N enriched NH_4^+ during spring and uptake of ^{15}N depleted NO_3^- during summer has also been reported in Lake Michigan (McCusker et al. 1999). Urban et al. (2004) also reported higher $\delta^{15}N$ during winter compared to summer in organic matter collected in sediment trap of Lake Superior and concluded seasonal shift in nutrient source for phytoplankton to be the most likely reason. Taken together, patterns in natural abundance $\delta^{15}N_{POM}$ in Lake Superior are consistent with earlier studies in the Great Lakes (McCusker et al. 1999; Urban et al. 2004; Kumar et al. 2008) and provides an insight into the seasonal nutrient utilization with predominantly NH_4^+ utilization during winter and relatively higher NO_3^- use during summer.

Transformation of organic matter in deep layers

Sediment trap studies show that degradation of organic particles (which broadly includes microzooplankton grazing, remineralization, protein hydrolysis, and loss of dissolved organic N) in the water column of the Great Lakes is very efficient (Eadie et al. 1984). Depleted N (molar C/N ratios 14–45) in sediment traps material in Lake Superior suggests degradation of organic matter during settling, leading to decrease in organic carbon fluxes with depth (Baker et al. 1991). Overall, approximately 75% of organic carbon settling from surface waters degrades in transit to the lake floor on the time scale of 1 year (Baker et al. 1991).

The depth-dependent variation in POM isotopic composition and concentration is an indicator of organic matter transformation (Altabet 1988). The decrease in PON concentration and increase in $\delta^{15}N_{POM}$ with depth during the present study may indicate oxidative decomposition of POM (Saino and Hattori 1980; Altabet and McCarthy 1986; Nakatsuka et al. 1992) and/or fragmentation of large sinking particles (Altabet 1988; Bacon et al. 1985; Saino 1992) along with possible food chain effects (Altabet 1988). Release of ^{14}N from POM due to degradation of organic matter during settling may result in increasing $\delta^{15}N_{POM}$ (Saino and Hattori 1980; Altabet and McCarthy 1986; Nakatsuka et al. 1992), whereas fragmentation of ^{15}N enriched sinking particles, mainly by product of zooplankton feeding (Minagawa and Wada 1984; Adams and Sterner 2000), may add to this effect. Given these processes, $\delta^{15}N_{POM}$ at depth is related to settling velocity of sinking particles. In a region where organic matter settling velocity is rapid due to formation of large particles in the surface, the $\delta^{15}N_{POM}$ in deeper layers have been found quite similar to surface $\delta^{15}N_{POM}$ (Minagawa et al. 2001). The lower settling velocity provides higher residence time in the water column for degradation and fragmentation of sinking particles leading to increased $\delta^{15}N_{POM}$. Settling velocities in Lake Superior (mass: 0.27–0.46 m day^{-1} and organic C: 0.49–1.00 m day^{-1}; Baker et al. 1991) are lower than in oceans (5–400 m day^{-1}; Alldredge and Gottschalk 1988; Turner 2002), probably providing enough time for fragmentation of sinking particles leading to observed higher $\delta^{15}N_{POM}$. In general, data from the present study indicates that the organic matter transformation in water column of Lake Superior is quite similar to oceans, consistent with previous sediment trap study (Baker et al. 1991). This is also consistent with the hypothesis of low organic matter supply to sediments leading to limited NO_3^- removal.

Role of rivers

Lake Superior is fed by several large and small rivers but organic matter contributions from these rivers are small compared to total organic matter in the lake (Thomas and Dell 1978; Halfon 1984; Cotner et al. 2004). Organic carbon loading from rivers (0.45–0.51×10^{11} mol year^{-1}; Cotner et al. 2004) represents only about 10% of the annual photoautotrophic production (3.6–8.6×10^{11} mol year^{-1}; Sterner 2010) in Lake Superior. Similarly, annual total N input to the lake, including rivers and precipitation, is around 6.6×10^9 mol year^{-1} ($\sim 1.8 \times 10^9$ mol year^{-1} of organic N from rivers; Sterner et al. 2007) compared to annual lake-wide total N uptake of 16.2×10^9 mol year^{-1} (Kumar et al. 2008).

In general, the coastal region of an aquatic system is characterized by mixed signatures from terrestrial and aquatic environment (Ostrom et al. 1997; Kumar et al. 2004). For example, in most of the oceanic systems, the average $\delta^{15}N_{POM}$ is often higher than the $\delta^{15}N_{POM}$ brought in by rivers leading to dilution and hence lowering of the $\delta^{15}N_{POM}$ in coastal and estuarine region (e.g., Mariotti et al. 1984; Kumar et al. 2004). In Lake Superior, however, overall average $\delta^{15}N_{POM}$ is lower than the riverine values, so that, the terrestrial inputs lead to increase in average POM isotopic composition at stations closer to the coast. But this increase was not statistically significant compared to open lake stations, which may be due to smaller particulate N contribution from riverine sources. Assuming observed mean PON (3.2 μM N) as representative particulate N concentration from rivers to the lake during May 2005, our calculations show that particulate N contribution from rivers to the lake during that period was only about 1% of the total annual organic N input (discharge during May 2005 $\sim 5.2 \times 10^9$ m^3; http://www.glerl.noaa.gov/). This suggests that much of N inputs from rivers to the lake are in dissolved form. However, our assessment of the role of riverine inputs in modifying the isotopic composition of POM in the lake may be partial due to limited temporal sampling of the rivers, which may not be entirely representative of the watershed dynamics. We suggest a thorough temporal sampling of riverine inputs to the lake to resolve its role in the lake's biogeochemistry.

Conclusions

This study presents a comprehensive analysis of spatial and temporal variability in isotopic composition of N in the POM of Lake Superior. Unlike many other previous studies that concentrated mostly on coastal regions or had very few open lake stations, the present study focused on wide temporal and spatial coverage of the lake. This study shows that on an annual basis NH_4^+ is the dominant source of nutrients for phytoplankton and bacteria with variable contribution from NO_3^-. The contribution of NO_3^- is higher during summer than winter. No significant effect of riverine organic matter was observed on isotopic composition of particulate matter in the lake during this study; however, more extensive temporal sampling of tributary rivers could more fully resolve this aspect. Depth-dependent variability in isotopic composition and concentration of particulate matter suggested transformation of organic matter with depth, which strengthens the hypothesis that lack of labile organic matter supply to the lake bottom decreases the NO_3^- removal potential in Lake Superior. Overall, this study along with a few other recent investigations of Lake Superior demonstrates the existence of a dynamic N cycle in the lake that contrasts with earlier understanding of its biogeochemical cycles.

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