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thesis entitled

Geochemical and Isotope Dynamics of
Dissolved Inorganic Nitrogen in
Grand Traverse Bay, Lake Michigan

presented by

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has been accepted towards fulfillment
of the requirements for

MS degree in Environmental Geoscience

Major professor

Date 8-12-99

GEOCHEMICAL AND ISOTOPE DYNAMICS OF DISSOLVED INORGANIC NITROGEN IN GRAND TRAVERSE BAY, LAKE MICHIGAN

By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Geological Sciences

1999

ABSTRACT

GEOCHEMICAL AND ISOTOPE DYNAMICS OF DISSOLVED INORGANIC NITROGEN IN GRAND TRAVERSE BAY, LAKE MICHIGAN

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Spatial and temporal variations in the $\delta^{15}N$ of NO_3^- in Grand Traverse Bay, Lake Michigan were explored to better understand sources of inorganic N to the bay and the effects of climate change on N cycling. The bay was thermally stratified approximately one month earlier in 1998 than in 1997. The $\delta^{15}N$ of NO_3^- showed minor seasonal variation in 1997; however, in 1998, a marked decline in the $\delta^{15}N$ of NO_3^- with time was observed. Although decreasing NO_3^- concentrations during the summer months indicated that NO_3^- uptake occurred during both seasons, isotopic fractionation consistent with uptake was not observed. Phytoplankton likely assimilated a combination of ^{15}N-enriched NH_4^+ and ^{15}N-depleted NO_3^- in 1997 and 1998, resulting in seston $\delta^{15}N$ values that were almost always higher than those of NO_3^-. Average seston $\delta^{15}N$ values in 1998 were 7‰ higher than values observed in 1997. The occurrence of ^{15}N-enriched seston in 1998 was linked to increased NH_4^+ uptake relative to NO_3^- assimilation by a smaller phytoplankton biovolume. Seston organic N is an important source of NO_3^- in Grand Traverse Bay; thus, rapid internal regeneration of NH_4^+ and NO_3^- from seston is a primary control on the $\delta^{15}N$ of inorganic N species. The $\delta^{15}N$ of seston appears to be sensitive to changes in the timing of thermal stratification and may therefore be an indicator of climate warming.

To my Family:

With your love, everything is possible.

ACKNOWLEDGMENTS

This work would not be possible without the support of Michigan SeaGrant (U/MC grant PO A31744 R/ES-16) and the US EPA (R825151-010). I would also like to thank the crews of the RV Lake Guardian, RV Shenehon, RV Laurentian, RV W. G. Jackson, and the late RV Northwestern for ship time and cheerful support. A great deal of gratitude goes to my advisor, Nathaniel Ostrom, and my committee members, Dave Long and Steve Hamilton, who answered endless questions and were always willing to explain things more than once. All of the Geochem lab crew--Robin, Eileen, Colleen, Mary, Tucker, and Andery--thanks for not getting too upset with all my experimentations and messes. Many thanks to my family outside of family, especially Ted, Tifani, and Tom in Vermont who provided the space I needed to finally write the first draft of this manuscript. Mom and Dad, thank you for always being supportive of me, even when I wasn't supportive of myself. Heather, dear sister, thank you for always being just a little bit crazier than I am.

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INTRODUCTION

Variations in climate can have a dramatic influence on the Great Lakes ecosystem by causing increases or decreases in precipitation (Montroy 1997), reduction in lake levels, altered frequency and timing of lake turnover, reduced ice cover (Hanson *et al.* 1992), increased likelihood of anoxia, and changes in water chemistry and biota (Mortsch and Quinn 1996). For example, during an ice-free winter, strong winds may result in the resuspension of P that would otherwise be trapped in sediments (Nicholls 1998). Long-term changes in water column stratification and nutrient sources, such as stream runoff and precipitation, may ultimately result in the perturbation of primary production and of interactions between trophic levels in the Great Lakes ecosystem. To better understand sources of inorganic N, the influences of dissolved inorganic nitrogen (DIN) on $\delta^{15}N$ at the base of a foodweb, and the effects of climate change on N cycling, we explored spatial and temporal variations in the isotopic composition of NH_4^+ and NO_3^- in Grand Traverse Bay, Lake Michigan. Strong El Niño years such as 1982-83, 1987, and 1992 have been associated with climatic changes in the Great Lakes (Nicholls 1998). Understanding the response of this ecosystem to such short-term climatic changes can enable a more accurate prediction of the response of aquatic systems to future climatic events.

N isotope ratios have been used to assess the origins of NO_3^- and NH_4^+ in terrestrial and aquatic environments (Liu and Kaplan 1989, Cifuentes *et al.* 1989, Macko and Ostrom 1994, Ostrom *et al.* 1997, Ostrom *et al.* 1998b). Sources of inorganic N to aquatic environments primarily include atmospheric deposition, fertilizers, sewage inputs,

N-fixation, and *in situ* remineralization and nitrification. Inputs of N from these sources may be distinguished if the sources are characterized by distinct $\delta^{15}N$ values. For example, low $\delta^{15}N$ values for NO_3^- and phytoplankton in coastal ecosystems and in Lake Superior have demonstrated the importance of atmospheric deposition as a source of N to primary production (Fogel and Paerl 1993, Paerl *et al.* 1993, Paerl and Fogel 1994, Ostrom *et al.* 1998b). Yoshioka *et al.* (1988) observed that $\delta^{15}N$ values of NO_3^- in Lake Kizaki and River Naka-Nögu were close to 0‰ while the $\delta^{15}N$ of NO_3^- in eutrophic Lake Suwa was 5.0 to 5.6‰. High $\delta^{15}N$ values for NO_3^- in Lake Suwa relative to values in Lake Kizaki and River Naka-Nögu were strongly indicative of a large contribution of NO_3^- from sewage. In the Truckee River, however, N inputs to phytoplankton via N-fixation could not be distinguished from fertilizer inputs because both of these N sources tend to have low and similar $\delta^{15}N$ values (Estep and Vigg 1985). Consequently, NO_3^- source differentiation based on $\delta^{15}N$ is dependent on the existence of sources with unique isotopic compositions and may be confounded by inputs from multiple sources.

Stable isotopic studies of biogeochemical reactions in natural environments are complicated by the fact that isotopic variation may be the result of numerous reactions and processes (Ostrom *et al.* 1998b). Spatial and temporal variation in the isotopic composition of DIN may occur because DIN is subject to isotopic fractionation during uptake by phytoplankton (Cifuentes *et al.* 1989, Waser *et al.* 1998). N uptake by phytoplankton is the rate-controlling step in an ecosystem when NH_4^+ or NO_3^- is the limiting nutrient. Little or no fractionation occurs during uptake under N limitation and the $\delta^{15}N$ of phytoplankton reflects that of its nutrient source (Wada and Hattori 1978,

Wada 1980). If concentrations of NO_3^- or NH_4^+ are not limiting, however, then the $\delta^{15}N$ of both the phytoplankton and the residual N may be altered. For example, assimilatory uptake of NH_4^+ or NO_3^- by phytoplankton or bacteria has been shown to leave the residual N enriched in ^{15}N by as much as 7‰ (Mariotti *et al.* 1984, Horrigan *et al.* 1990, Hoch *et al.* 1996). The direction of an isotope shift can also be used to reveal the predominant biological and microbial processes affecting DIN. For example, high and low $\delta^{15}N$ values for NO_3^- can be used to recognize regions of denitrification and nitrification, respectively (Cline and Kaplan 1975, Mariotti *et al.* 1981, Cifuentes *et al.* 1989, Liu and Kaplan 1989, Horrigan *et al.* 1990, Hedin *et al.* 1998).

The study of isotopic variation at the base of foodwebs is essential toward an understanding of N sources supporting foodwebs and trophic relationships. For example, Van Dover *et al.* (1992) used stable N isotopes to demonstrate that sewage was a nutritional support for a deep-sea foodweb. Isotopic studies of trophic relationships often make assumptions about the number of trophic levels present in a food web based on differences in $\delta^{15}N$ between primary producers and predatory fish (e.g., Cabana and Rasmussen 1996). The ultimate control of foodweb $\delta^{15}N$, however, is not the isotopic composition of the primary producers but that of the inorganic N assimilated by primary producers. Thus, variation of the $\delta^{15}N$ of consumers in different aquatic systems may be a result of different $\delta^{15}N$ values for DIN, and comparisons between these foodwebs without an understanding of the corresponding inorganic N isotope values may be misleading. Furthermore, the $\delta^{15}N$ of suspended organic material (seston) is likely to

change on a seasonal basis and depends at least in part upon the relative use of NO_3^- and NH_4^+ by phytoplankton (McCusker *et al.* 1999).

The relative use of different inorganic N species by primary producers over time may be affected by changes in climate such as El Niño events. For example, longer stratified periods and decreased epilimnetic nutrient availability may cause Lake Michigan phytoplankton populations to shift from the present diatom- and phytoflagellate-dominated communities (Fahnenstiel and Scavia 1987) to communities composed primarily of blue-green algae (Chang and Rossman 1988) or other phytoplankton species which are better adapted to low nutrient concentrations. Alterations at the base of a food web, as well as changes in the number of trophic levels present in that food web, may occur as a result of climate change and can be accurately documented using stable N isotopes. The present study explores spatial and temporal variations in the $\delta^{15}N$ of NH_4^+ and NO_3^- in Grand Traverse Bay, Lake Michigan, in order to better understand the relationship between DIN and nutrients at the base of the foodweb and to explore the effects of climate change on N cycling.

METHODS

Field methods

Water samples and conductivity-temperature-depth profiles were taken at two stations, GT1 (44° 50.00 N, 85° 37.00 W; 98 m depth) and GT3 (44° 59.00 N, 85° 34.80 W; 112 m depth), in Grand Traverse Bay, Lake Michigan (Figure 1). Eight cruises were conducted between April and September 1997 and seven cruises were performed between March and September 1998. A Seabird SBE-25 conductivity-temperature-depth profiler equipped with a fluorometer and transmissometer (Seatech) was deployed initially at each station to assess the physical and biogeochemical characteristics of the water column. Water samples were collected using 8 L or 5 L Go-Flo or lever-action Niskin bottles (General Oceanics), respectively, at 5-6 depths, including points above, within, and below the chlorophyll maximum. Each sample was filtered through a precombusted (500 °C, 2 hours) 0.45 μm glass fiber filter (Whatman GF/F) and transferred to acid-washed Nalgene bottles. Samples were stored on ice, frozen within 12 hours of collection, and stored frozen (-20°C) until analysis.

Water column characteristics

Concentrations of NO_3^- in water samples were determined by suppressor-based anion chromatography (Shipgun and Zolotov 1988) using a Rainin HPLC with conductivity detection (LDC Analytical). A Dionex IonPac (AS4A-SC) column and a 2.4 mM $Na_2CO_3/NaHCO_3$ eluent were used to separate anions. Concentrations of NH_4^+ were measured using an Orion (model 95-12) ion specific electrode (Garside *et al.* 1978,

Ostrom *et al.* 1998b). The accuracy and limits of detection for both techniques were approximately 0.1 μM (Ostrom *et al.* 1998a). Soluble reactive P (SRP) analysis was conducted on filtered samples, and concentrations were determined colorimetrically as molybdate reactive P (Murphy and Riley 1962). The accuracy and limit of detection of SRP analysis was approximately 0.01 μM.

Isotopic analysis of NO_3^- and NH_4^+

Purification of NH_4^+ and NO_3^- from water samples for stable isotopic analysis was conducted using a steam distillation procedure (Bremner and Keeney, 1966; Velinsky *et al.*, 1989; Ostrom, 1992; Ostrom *et al.*, 1998a). An initial distillation was performed to recover and purify NH_4^+ for isotopic analysis. Sample volumes were optimized to recover between 1 and 20 μmol N. Sample pH was adjusted to > 10 by the addition of 2.0 mL 5 N NaOH (previously distilled to remove NH_4^+) to convert NH_4^+ to volatile NH_3 gas. The collection rate was adjusted to 11.0 mL/minute, and the condensate from the distillation was passed through an Erlenmeyer trap flask containing 25 mL of 0.084 N HCl. If the sample contained less than 0.5 μmol NH_4^+, the trap flask solution was discarded because this small amount of NH_4^+ could not be accurately analyzed for $\delta^{15}N$. Immediately following the distillation for NH_4^+, 0.3 g of finely ground Devarda's alloy (50% Cu, 45% Al, 5% Zn) was added to the sample in order to reduce NO_3^- to NH_4^+. The Erlenmeyer trap flask was replaced with a clean flask containing the same volume and concentration of HCl as discussed above, and the sample was distilled a second time as previously described. The NH_4^+ in the condensate was bound onto 0.1 g of a zeolite

molecular sieve (Union Carbide Ionsiv W-85), which exchanges H^+ for NH_4^+ (Velinsky *et al.* 1989). Optimal binding conditions involve adjusting the sample pH to 5.0, adding 0.1 g of the sieve, and stirring gently for 30 minutes (Ostrom *et al.* 1998a). The zeolite was then filtered onto a precombusted glass fiber filter (Whatman GF-F) and dried overnight at 40°C. The binding procedure was repeated twice to insure complete recovery of NH_4^+, and the two filters were combined as one sample and prepared for combustion. In preparation for combustion, the samples were transferred to precombusted quartz tubes and mixed with ca. 3 g each of precombusted (850°C, 4 h) copper and copper oxide and sealed under vacuum. Samples were combusted using a modified Dumas procedure (Macko 1981), after which they were cryogenically purified and analyzed for isotopic abundance using a Micromass Prism mass spectrometer. Distillation of deionized water yielded a background contribution of 0.4 μmol N with a $\delta^{15}N$ of $+8.0 \pm 1.3‰$ derived primarily from the Devarda's alloy; consequently, all $\delta^{15}N$ values of NO_3^- were corrected for this background contribution using a mass balance equation (Ostrom 1992). Background levels of NH_4^+ from the distillation of deionized water without the addition of Devarda's alloy were negligible. Maintenance of isotopic integrity through the distillation process was demonstrated by analysis of an international NO_3^- standard, IAEA N-3, which has a reported value of 4.72‰ (Bohlke and Coplen 1995). Analysis of three replicates of the IAEA N-3 standard in our laboratory yielded a $\delta^{15}N$ value of $4.1 \pm 0.1‰$. Precision of replicate samples was $\leq 0.5‰$.

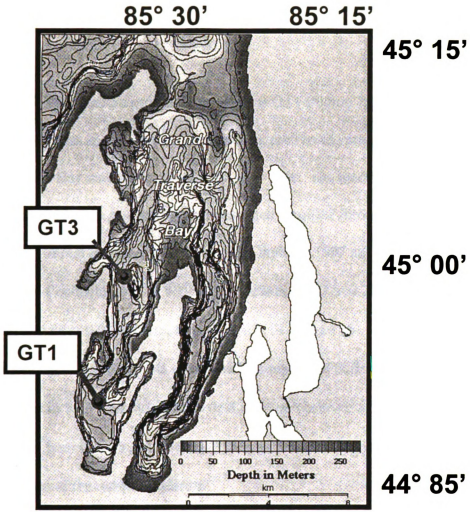


Figure 1: Map of Grand Traverse Bay, Lake Michigan (http://www.glerl.noaa.gov)

RESULTS

1997

Temperature profiles from stations GT1 (Figure 2a) and GT3 (Figure 3a) during the 1997 season were indicative of a cold, protracted spring. Stratification in Grand Traverse Bay was not apparent until early June. The thermocline was well-developed at a depth of 15 m in July and the bay remained stratified through September. The entire water column remained oxic throughout both the 1997 and 1998 sampling seasons.

Concentrations of SRP ranged between 0.07 to 0.22 μM at station GT1 (Figure 2b) and from 0.08 to 0.20 μM at station GT3 (Figure 3b). Spring SRP concentrations were generally higher than concentrations measured during the summer months. A sharp decline in SRP from 0.16 μM to 0.08 μM was observed following stratification in early June at both stations, after which SRP concentrations remained low (ca. 0.08 μM) for the duration of the sampling season.

Chlorophyll fluorescence ranged from 0.1 to 1.1 relative fluorescence units (RFU) at station GT1 (Figure 2c) and from 0.1 to 1.5 RFU at station GT3 (Figure 3c) throughout the sampling season. Extensive mixing of the water column was reflected by relatively high chlorophyll fluorescence readings (0.6 - 0.7 RFU) throughout the water column during April, May, and early June 1997. After stratification in early June, chlorophyll fluorescence was generally lower and a maximum tended to occur just below the thermocline.

Concentrations of NH_4^+ ranged from 0 - 1.3 μM at station GT1 (Figure 2d) and 0 - 1.1 μM at station GT3 (Figure 3d) throughout the season; however, the lowest NH_4^+

concentrations occurred throughout the water column in the early spring and in September. Maximum concentrations of 1.0 to 1.3 μM at both stations occurred in the lower water column in late July through early August. Gradually increasing NH_4^+ concentrations (from 0.5 to ca. 1.1 μM) in the lower water column were observed following a sharp decline in SRP concentrations at both stations.

Concentrations of NO_3^- ranged from 12.6 to 18.7 μM at station GT1 and from 12.8 to 17.4 μM at station GT3 during the 1997 sampling season (Figure 4a and 4b, respectively). The small variation in NO_3^- concentration throughout the water column in May and early June at both stations (15.8 ± 0.8 μM at GT1 and 15.6 ± 0.7 μM at GT3) was indicative of extensive water column mixing. Declining NO_3^- concentrations in the upper water column at Station GT1 (15.0 to 12.6 μM) and at Station GT3 (15.5 to 12.8 μM) between July and September were likely a result of NO_3^- uptake by phytoplankton. Concentrations of NO_3^- in the lower water column remained relatively constant (ca. 16 μM) at both stations throughout the sampling season.

The isotopic composition of NO_3^- ranged from +0.4‰ to +7.8‰ at Station GT1 over the course of the 1997 sampling season (Figure 4c). The small degree of variation in $\delta^{15}N\text{-}NO_3^-$ (less than 1‰) observed at both stations in May 1997 was consistent with extensive water column mixing. At Station GT1 in mid-June and early July, the $\delta^{15}N$ of NO_3^- tended to be more ^{15}N-enriched throughout the water column (+4.0 to +7.8‰) relative to the rest of the sampling season. A general decline in $\delta^{15}N$ values of NO_3^- (to +3.5 to +0.5‰) was observed throughout most of the water column in mid-July through September. The $\delta^{15}N$ of NO_3^- at station GT3 ranged from +0.4‰ to +6.1‰; however,

there were no easily discernable seasonal trends in $\delta^{15}N\text{-}NO_3^-$ at GT3 during the 1997 season (Figure 4d).

The $\delta^{15}N$ of NH_4^+ was higher than that of NO_3^- whenever sufficient NH_4^+ was available to facilitate the measurement of its isotopic composition. The $\delta^{15}N$ of NH_4^+ ranged from +8.6‰ to +17.2‰ at GT1 (n = 19) and +10.3‰ to +17.5‰ at GT3 (n = 11). Sufficient data to clearly resolve temporal or seasonal trends in the isotopic composition of NH_4^+ were not available owing to the small concentrations of NH_4^+ present in Grand Traverse Bay.

Seasonal variations in the isotopic composition of NO_3^- throughout the water column were described using the following relationship, which weights the $\delta^{15}N$ of NO_3^- at each sampling depth by its respective concentration (Ostrom *et al.* 1997):

$$\delta^{15}N_w = \frac{\sum_{i=1}^{n} C_i * \delta_i}{\sum_{i=1}^{n} C_i} \qquad (1)$$

where $\delta^{15}N_w$ is equal to the N isotopic composition of NO_3^- or seston (in ‰) weighted by concentration at a station on a specific date, C_i corresponds to the concentration of NO_3^- or seston organic N for an individual sample (μM), δ_i is equal to the $\delta^{15}N$ of an individual NO_3^- or seston sample (‰), and n is the number of NO_3^- or seston samples collected at a station on a particular date.

The concentration-weighted $\delta^{15}N$ of NO_3^- at station GT1 increased from +2.8‰ to +5.3‰ between May and mid-June, then gradually decreased to +1.4‰ in September (Figure 5a). There was no easily discernible seasonal trend in the weighted $\delta^{15}N$ of NO_3^- at station GT3 during the 1997 sampling season, and values ranged from +2.1‰ to

+4.3‰ (Figure 5b). In contrast, the concentration-weighted $\delta^{15}N$ of seston at station GT1 (Figure 5c) decreased gradually from +5.9‰ in early May to +1.9‰ in August, then increased to +6.4‰ in mid-September. The weighted $\delta^{15}N$ of seston at station GT3 (Figure 5d) also decreased from +6.1 to +3.6‰, then increased dramatically to +9.2‰ in September. While there was a significant relationship between the seasonal trends of the weighted isotopic composition of NO_3^- and that of seston at station GT1 ($\alpha = 0.05$, $p = 0.46$, $n = 7$) in 1997, such a relationship was not present at station GT3 ($\alpha = 0.05$, $n = 6$).

1998

In 1998, temperature profiles were indicative of an early, warm spring (Figure 6a). The bay showed signs of stratification as early as May 7, and was well-stratified from mid-May through September. During most of the sampling season, the thermocline was apparent near 15 m, but in mid-September a deeper (ca. 25 m) and more gradual thermocline was observed.

SRP concentrations were slightly lower (0.07 to 0.16 μM) at station GT3 in 1998 than in 1997 (Figure 6b), although a similar seasonal trend of rapidly decreasing SRP concentrations (0.10 to 0.07 μM) concurrent with stratification was observed. In 1998, P decline was apparent in early May; however, a similar rapid decline in SRP concentrations did not occur until late June of 1997.

Lower chlorophyll fluorescence values (0.10 - 0.85 RFU) were generally observed at station GT3 during the 1998 sampling season (Figure 6c), although the overall trend in chlorophyll fluorescence was similar to that observed in 1997. Water column mixing was apparent in March as shown by consistent values with depth (ca. 0.5 RFU). During May

and June, the highest chlorophyll fluorescence levels (0.65 - 0.85 RFU) occurred in a broad peak just beneath the thermocline. In August and September 1998, however, a chlorophyll fluorescence maximum occurred above the thermocline.

Concentrations of NH_4^+ were slightly higher (0 - 1.5 μM) at station GT3 during the 1998 sampling season (Figure 6d). As in 1997, increased NH_4^+ concentrations (1.0 to 1.4 μM) were generally observed in deeper waters following stratification, and the lowest concentrations were observed throughout the water column in March and in September.

Concentrations of NO_3^- ranged from 10.9 to 17.7 μM at station GT3 throughout the 1998 sampling season (Figure 7a). A decreasing trend in NO_3^- concentration throughout the upper water column during the summer months was observed in 1998, although the magnitude of the decline (15.5 μM to 11.0 μM) was greater than the decline observed in 1997. Concentrations of NO_3^- in the lower water column increased from 16.2 μM in March to 17.7 μM in mid-September of 1998.

The $\delta^{15}N$ of NO_3^- (Figure 7b) ranged from -1.3‰ to +7.6‰ at Station GT3 over the course of the 1998 sampling season. During March 1998, the $\delta^{15}N$ of NO_3^- was relatively high, and declined gradually throughout the water column from May through August, reaching a low of -1.3‰ at 25 m on August 7. Subsequently, the $\delta^{15}N$ of NO_3^- began to increase and attained values near +4.5‰ in September.

Concentration-weighted average $\delta^{15}N$ values for NO_3^- (Figure 8a) were strikingly more variable seasonally at station GT3 in 1998 than in 1997. The weighted $\delta^{15}N$ of NO_3^- exhibited a decreasing trend from +5.1‰ in May 1998 to +0.2‰ in August, followed by a slight increase to +3.8‰ in mid-September. The concentration-weighted

average $\delta^{15}N$ of seston (Figure 8b) was much higher overall in 1998 than in 1997, with a range of 8.8‰ to 13.7‰. A strong relationship exists between the weighted isotopic composition of seston and that of NO_3^- in 1998 ($\alpha = 0.05$, $r^2 = 0.87$, $n = 7$), whereas in 1997 there was no significant relationship between the weighted $\delta^{15}N$ of NO_3^- and that of seston at station GT3. The isotopic composition of NH_4^+ (range of 7.0 to 20.9‰, $n = 20$) remained higher than that of NO_3^- at all times in 1998; however, the data were not complete enough to allow the delineation of seasonal trends.

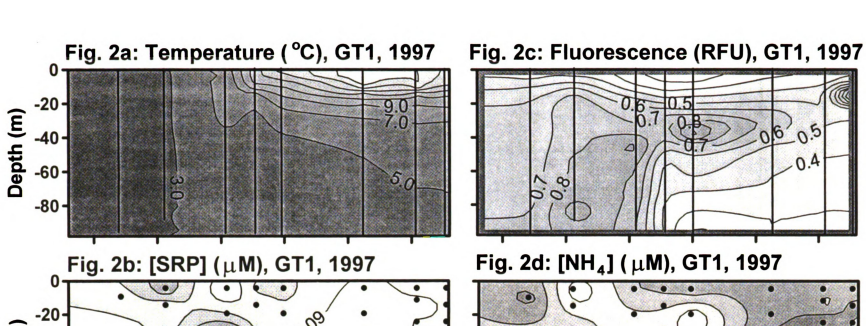


Figure 2: Water column temperatures (°C), soluble reactive phosphorous (SRP) concentrations (μM), chlorophyll fluorescence (RFU), and NH_4^+ concentrations (μM) plotted as a function of depth (m) and sampling date for station GT1 during the 1997 sampling season. Vertical lines and points (•) represent both sampling dates and the depth interval over which samples were taken.

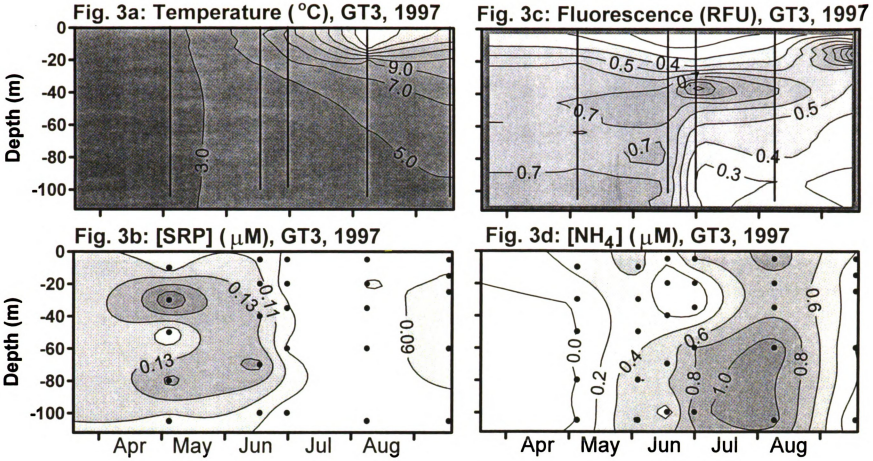


Figure 3: Water column temperatures (°C), soluble reactive phosphorous (SRP) concentrations (μM), chlorophyll fluorescence (RFU), and NH_4^+ concentrations (μM) plotted as a function of depth (m) and sampling date for station GT3 during the 1997 sampling season. Vertical lines and points (•) represent both sampling dates and the depth interval over which samples were taken.

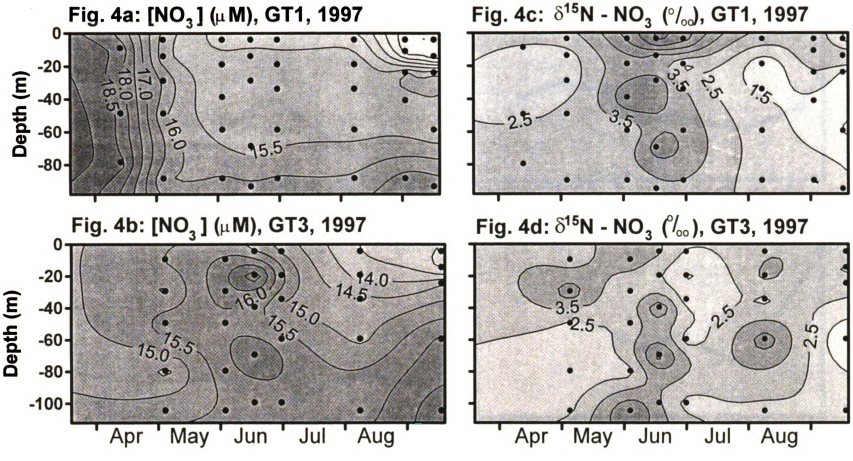


Figure 4: Concentrations of NO_3^- (μM) and $\delta^{15}N$ values of NO_3^- (‰) plotted as a function of depth (m) and sampling date for stations GT1 and GT3 during the 1997 sampling season. Points (•) represent both sampling dates and the depth interval over which samples were taken.

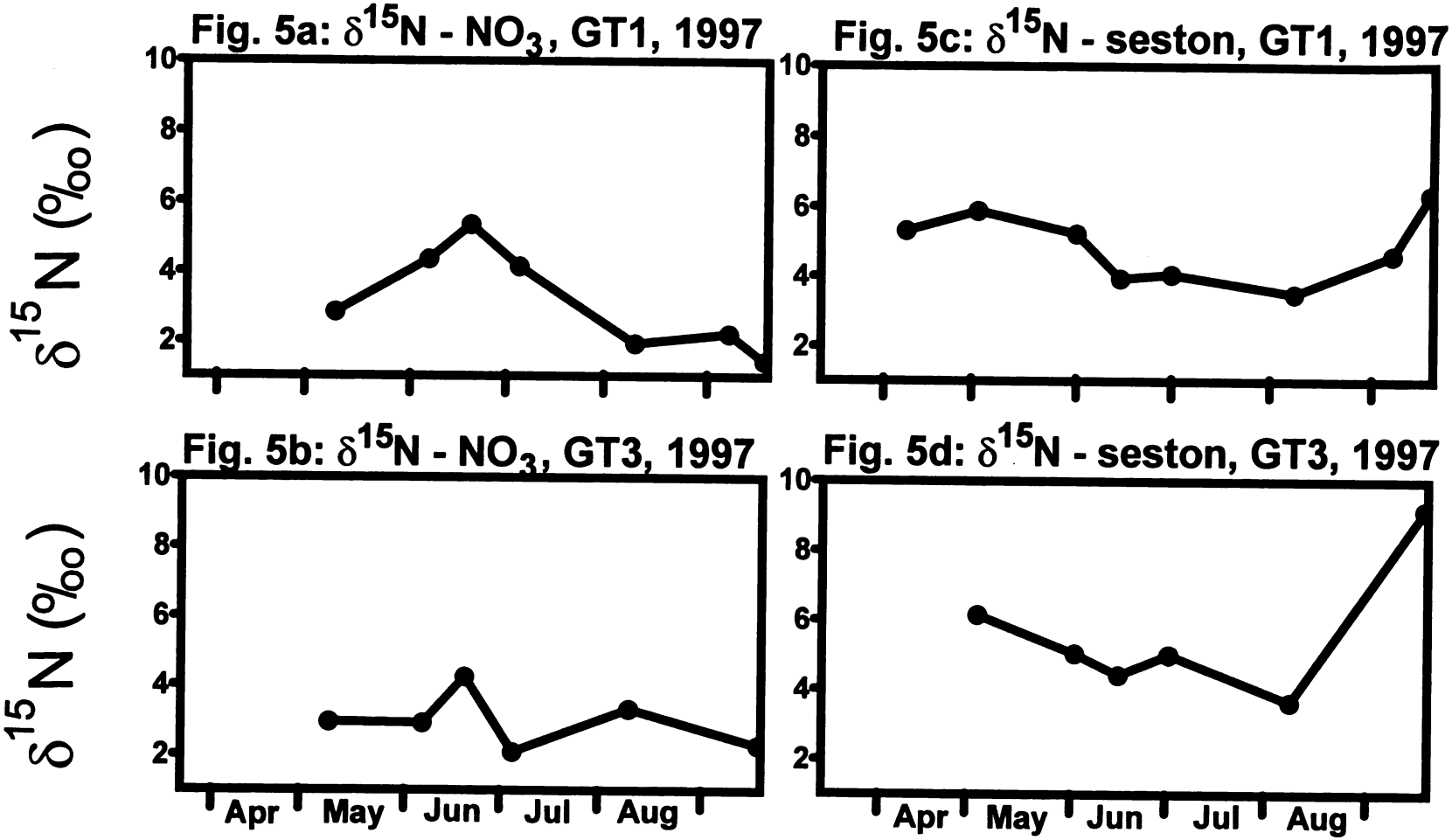


Figure 5: Concentration weighted average $\delta^{15}N$ values (‰) for NO_3^- and seston plotted as a function of sampling date at Stations GT1 and GT3 during the 1997 sampling season.

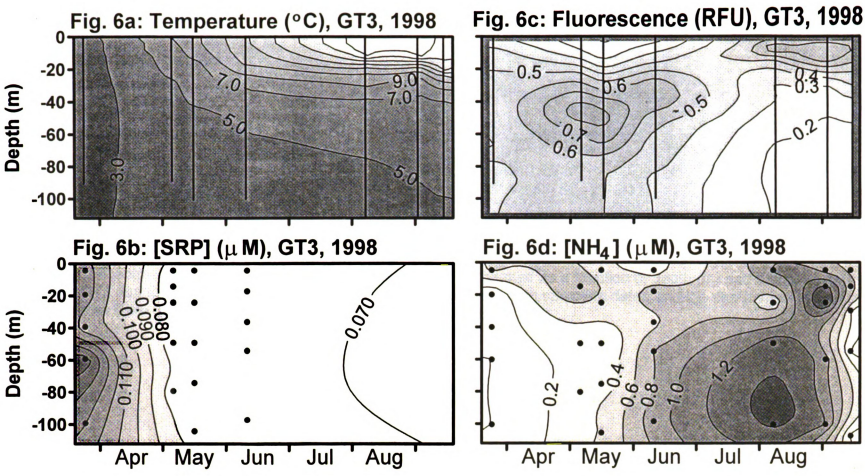
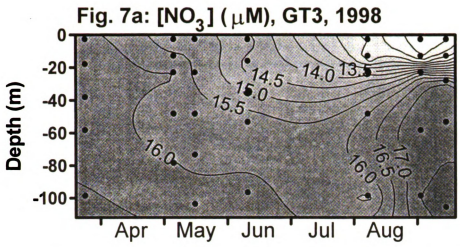


Figure 6: Water column temperatures (°C), soluble reactive phosphorous (SRP) concentrations (μM), chlorophyll fluorescence (RFU), and NH_4^+ concentrations (μM) plotted as a function of depth (m) and sampling date for station GT3 during the 1998 sampling season. Vertical lines and points (•) represent both sampling dates and the depth interval over which samples were taken.



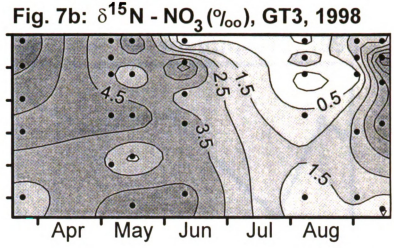


Figure 7: Concentrations of NO_3^- (μM) and $\delta^{15}N$ values of NO_3^- (‰) plotted as a function of depth (m) and sampling date for station GT3 during the 1998 sampling season. Points (•) represent both sampling dates and the depth interval over which samples were taken.

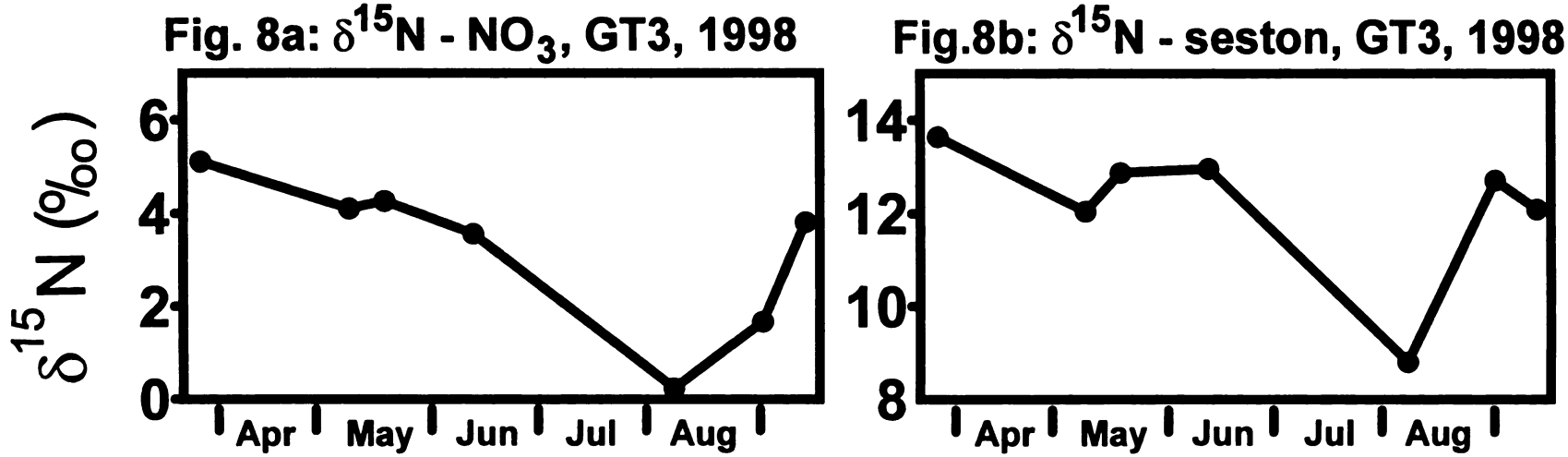


Figure 8: Concentration weighted average $\delta^{15}N$ values (‰) for NO_3^- and seston plotted as a function of sampling date at station GT3 during the 1998 sampling season.

DISCUSSION

Sediment resuspension and SRP dynamics

The highest SRP concentrations were observed during the unstratified period in both 1997 and 1998 (Figures 2b, 3b, 6b). This relatively large pool of available P is likely the result of sediment resuspension during winter mixing. Resuspension can be regarded as a mechanism which accelerates the flux of solutes between sediment and lake water, both in the sense of increasing flux of organic P from sediment to water and in increasing the introduction of O_2 and other oxidizing elements from water to sediment (Søndergaard *et al.* 1992). In the open waters of Lake Michigan, water column trends of SRP and total P were generally similar, although TP was always higher than SRP (Eadie *et al.* 1984). Higher SRP and TP concentrations in the benthic nepheloid layer relative to the rest of the water column further support the idea of a source of SRP originating from the resuspension of sediments. Sediment resuspension tends to be greatest in Lake Michigan during the winter months and therefore may control total P and SRP concentrations in early spring (Chambers and Eadie 1981). The large amount of winter resuspension is a mechanism that provides a greater amount of contact between recent sediments and the water column and thus loads the lake with P (Eadie *et al.* 1984). Sediment resuspension during the winter months may explain the relatively high SRP concentrations observed in Grand Traverse Bay prior to stratification in both 1997 and 1998. The analysis of sediment trap material from the bay, however, is not yet complete.

The importance of winter water column mixing to spring P concentrations in the water column was demonstrated by the observation that when ice cover inhibits winter

mixing of Lake Michigan, spring total P concentrations are significantly less than in years without ice cover (Rodgers and Salisbury 1981). In Grand Traverse Bay during the spring of 1998, however, lower SRP concentrations were recorded following a winter with no observable ice cover than following the winter of 1996-1997 when significant ice cover was observed (Table 1). Lower spring P concentrations in the water column prior to stratification in 1998 may be the result of the occurrence of fewer major storm events contributing to extensive mixing during the winter of 1997-98 and early spring stratification in 1998.

Sedimentation plays a major role in the decline of P concentrations during stratified periods and is influenced by plankton community structure (Guy *et al.* 1994). Diatoms, a major component of the spring phytoplankton community in Lake Michigan, are characterized by relatively high sedimentation losses during early stratification. This sinking loss is important in removing diatoms and associated nutrients from the epilimnion (Fahnenstiel and Scavia 1987). Evidence of rapid nutrient removal from the water column was observed in Grand Traverse Bay. During 1997, SRP concentrations were generally higher during the unstratified period, and a decline in SRP concentrations was not apparent until 2-3 weeks following stratification. In 1998, however, SRP concentrations declined throughout the water column even before stratification was strongly developed, suggesting that much less P was available to support the phytoplankton population.

Sediment resuspension may control SRP concentrations in the water column during unstratified periods, but resuspension in deeper waters during stratification cannot contribute to primary production in the epilimnion (Conley *et al.* 1988). During stratified

periods, additional P may be supplied to the water column via external sources including surface runoff, stream inputs, atmospheric deposition, and sediment fluxes. In Lake Michigan, however, the annual P utilization for primary production is about 100 times greater than the estimated SRP sediment flux and 57 times greater than the combined external loadings of total P (Conley *et al.* 1988). Thus, internally regenerated P is necessary to sustain the rates of primary production commonly observed in Lake Michigan during stratified periods, and the internal regeneration of P must occur on very short time scales in the water column (Conley *et al.* 1988).

The timing and strength of stratification had a dramatic effect on P (SRP) availability to primary producers in Grand Traverse Bay. During 1997, when the bay experienced an exceptionally cold and protracted spring, the water column remained unstratified until early June. The lack of stratification during this long period may have resulted in greater sediment resuspension and higher SRP concentrations in the water column. In 1998, however, a warm spring and early stratification may have inhibited resuspension and therefore less P was available to support the phytoplankton population.

N Sources and Processes in Grand Traverse Bay

External sources of DIN to Grand Traverse Bay may include atmospheric deposition, stream inflows, groundwater, and exchange with the open waters of Lake Michigan. Inputs of NH_4^+ and NO_3^- to surface waters via atmospheric deposition in 1997 were calculated using NADP / NTN monthly precipitation-weighted mean concentrations from the Wellston, MI station (http://nadp.sws.uiuc.edu/nadpdata). Atmospheric deposition of NH_4^+ and NO_3^- combined accounted for less than 1% of the total mass of

DIN in the bay during the 1997 sampling season; thus, precipitation was not considered to be a significant external DIN source in this model. Inputs of NO_3^- from the Boardman River, the major riverine source to the west arm of Grand Traverse Bay, accounted for only 0.005% to 0.02% of the total mass of DIN in the bay from May to October of 1998 (S. Woodhams, personal communication). Contributions of DIN to the bay from groundwater were also likely to be minimal relative to the bay's volume (D. Boutt, personal communication). Water exchange between Grand Traverse Bay and Lake Michigan is limited by the presence of a shallow sill at the north end of the bay (Lauff 1957), and currents in the bay are weak relative to those in the open waters of the lake (G. Miller and T. Miller, GLERL, unpublished data). Consequently, internal regeneration of NH_4^+ and NO_3^- is more likely to control the $\delta^{15}N$ of DIN species than are external sources of DIN to the bay.

N fixation is a potentially significant source of ^{15}N-depleted N. The mineralization and nitrification of N_2-fixing algae may yield NO_3^- with low $\delta^{15}N$. Therefore, N fixation is a mechanism that may cause seasonal variation in the $\delta^{15}N$ of NO_3^-. N fixation may occur at NO_3^- concentrations greater than 10 μM but is significantly inhibited by NH_4^+ concentrations as low as 0.5 μM (Takahashi and Saijo 1988). In Grand Traverse Bay, NH_4^+ concentrations below 0.5 μM did not occur at any time in the epilimnion during August and early September of 1997 or 1998, when the lowest $\delta^{15}N$ values for NO_3^- were observed. Furthermore, in oligotrophic Lakes Superior, Huron, and Michigan, biological N fixation accounts for only 0.02% of total N inputs to

these systems (Mague and Burris 1973). Thus, N fixation is not likely to be a source of ^{15}N-depleted NO_3^- to Grand Traverse Bay.

Sediments may serve as either a net source or a net sink for NO_3^-, depending upon the conditions that exist in a specific sedimentary environment. Denitrification in Lake Michigan sediments was found to be an unlikely sink for NO_3^- dissolved in hypolimnetic water overlying the sediments; however, this process was a sink for N mineralized in the sediments (Gardner *et al.* 1987). Recent work in estuarine sediments suggests that even if sediments are a sink for hypolimnetic NO_3^-, isotopic evidence for sediment denitrification would not be observed in the overlying waters (Brandes and Devol 1997). Consequently, sediments in Grand Traverse Bay are not likely to be a significant source of NO_3^- to overlying waters, nor is sediment denitrification likely to influence the $\delta^{15}N$ of hypolimnetic NO_3^-.

The isotopic composition of NO_3^- is often controlled by uptake in aquatic systems (Saino and Hattori 1980, Mariotti *et al.* 1984, Cifuentes *et al.* 1988, Montoya *et al.* 1990, Altabet *et al.* 1991). During assimilation of NO_3^- or NH_4^+ by phytoplankton, decreasing DIN concentrations are usually observed concurrent with an increase in the $\delta^{15}N$ of the residual DIN. While decreasing NO_3^- concentrations were observed in the upper water column of Grand Traverse Bay following stratification in 1997 and in 1998, concurrently increasing $\delta^{15}N$ values for NO_3^- were generally not observed. Thus, NO_3^- uptake by phytoplankton is not a dominant factor influencing the isotopic composition of NO_3^- in this system. Similarly, Cifuentes *et al.* (1988) did not observe fractionation effects during uptake when NH_4^+ concentrations were below 20 μM in the Delaware Estuary, suggesting

that isotopic fractionation during uptake may not be observed below a critical concentration.

N inputs from external sources, N fixation, or sediments are not likely to affect the $\delta^{15}N$ of NO_3^- in Grand Traverse Bay. Although evidence of NO_3^- uptake by phytoplankton was observed, assimilation does not appear to strongly affect the $\delta^{15}N$ of NO_3^- in this system. Consequently, internal recycling of N via remineralization of organic matter and nitrification is likely a primary control on the $\delta^{15}N$ of NO_3^- in Grand Traverse Bay.

P controls on N dynamics

In 1997 and 1998, NH_4^+ concentrations gradually increased with time following the sharp decline in SRP concentrations. Higher NH_4^+ concentrations in the lower water column during July and early August in both years were also associated with changes in the pattern of chlorophyll fluorescence throughout the water column. Before stratification, NH_4^+ concentrations were generally low and chlorophyll fluorescence values were relatively high throughout the water column. A relatively large phytoplankton population was being mixed throughout the water column during the unstratified period, and this population likely assimilated a large proportion of the available NH_4^+. After stratification, water column mixing was greatly reduced. Changes in the availability of NH_4^+ to phytoplankton in the water column occurred as a result of reduced mixing following stratification. The amount of available NH_4^+ in aquatic systems is controlled by a balance of losses due to nitrification and uptake and inputs due to internal regeneration (Axler *et al.* 1982, Laird *et al.* 1988). The observation of low

NH_4^+ concentrations in the upper water column of Grand Traverse Bay indicates that following stratification, NH_4^+ uptake was more rapid than the remineralization of organic N. Higher NH_4^+ concentrations in the lower water column suggested that there was more regeneration of NH_4^+ than uptake. The apparent relationship between [NH_4^+] and [SRP] is likely a function of phytoplankton growth limitation by P and a relaxation of NH_4^+ uptake relative to remineralization once P becomes limiting, particularly in deeper waters following stratification.

In many freshwater aquatic systems, NH_4^+ is the preferred DIN species for uptake by phytoplankton (Takahashi and Saijo 1981, Axler *et al.* 1982, McCarthy *et al.* 1982, Gu and Alexander 1993, Takahashi *et al.* 1995). Because most phytoplankton prefer NH_4^+, NO_3^- uptake may be significantly inhibited at NH_4^+ concentrations as low as 0.5 μM (Takahashi and Saijo 1981, Priscu and Priscu 1984). In oligotrophic Flathead Lake, however, low rates of NO_3^- uptake occurred during most of the year at NH_4^+ concentrations of up to 5 μM (Dodds *et al.* 1991). Consequently, because NH_4^+ concentrations in Grand Traverse Bay were generally less than 2 μM, it is likely that phytoplankton assimilated both NH_4^+ and NO_3^- in varying proportions throughout 1997 and 1998.

Variations in the N isotopic composition of seston are primarily understood to reflect isotope effects associated with nutrient uptake by phytoplankton (Saino and Hattori 1980, Mariotti *et al.* 1984, Montoya 1990, Nakatsuka *et al.* 1992). When uptake by phytoplankton is a dominant control on the $\delta^{15}N$ of seston, low seston $\delta^{15}N$ values are observed concurrent with a sharp decrease in NO_3^- concentrations (Saino and Hattori

1980). High $\delta^{15}N$ values for seston relative to NO_3^-, however, may be a consequence of several processes, including assimilation of ^{15}N-enriched NH_4^+, losses of ^{15}N-depleted material from seston, microzooplankton grazing, and microbial degradation. Seston $\delta^{15}N$ values in Grand Traverse Bay were almost always higher than those of NO_3^- in both 1997 and 1998, thus providing isotopic evidence for the suggestion that phytoplankton assimilated a combination of ^{15}N-enriched NH_4^+ and ^{15}N-depleted NO_3^- throughout both sampling seasons.

In central Lake Michigan, the vertical distribution of phytoplankton biovolume was quite similar to the vertical distribution of chlorophyll (Brahce 1980). Thus, chlorophyll fluorescence may be used in some cases as a rough approximation of phytoplankton biovolume. Integrated chlorophyll fluorescence values at both stations GT1 and GT3 in 1997 were higher than values recorded in 1998 (Figure 9). Relatively low seston $\delta^{15}N$ values in Grand Traverse Bay throughout most of the 1997 sampling season were likely the result of the assimilation of both ^{15}N-enriched NH_4^+ and ^{15}N-depleted NO_3^- by a relatively large phytoplankton biovolume. The decreasing trend in concentration-weighted $\delta^{15}N$ values of seston observed in 1997 reflected increasing assimilation of ^{15}N-depleted NO_3^- as the sampling season progressed. In 1998, however, there was less P available to phytoplankton (as a result of early stratification). Phytoplankton biovolume, as reflected by chlorophyll fluorescence, was smaller overall because of reduced P availability (Figure 9). Higher $\delta^{15}N$ values for seston in 1998 relative to 1997 may be a result of less overall demand for inorganic N by phytoplankton. Higher proportions of ^{15}N-enriched NH_4^+ uptake by phytoplankton in 1998 relative to

1997 may have contributed to the marked increase in the $\delta^{15}N$ of suspended organic material between the two years.

The $\delta^{15}N$ of seston in Grand Traverse Bay appears to be largely controlled by a balance between uptake of ^{15}N-enriched NH_4^+ and ^{15}N-depleted NO_3^-. Furthermore, isotopic fractionation during uptake of NH_4^+ and NO_3^- in Grand Traverse Bay is minimal, although fractionation due to degradative processes affecting seston cannot be ruled out. Changes in the timing of stratification between 1997 and 1998 caused a subtle shift in P availability, and this markedly affected the timing of phytoplankton reliance on NH_4^+ versus NO_3^- as reflected in the $\delta^{15}N$ of seston in Grand Traverse Bay. The chain of events described in the bay is an illustration of how $\delta^{15}N$ at the base of a food web may be affected by longer stratified periods as a result of climate warming. Here, a longer stratified period in 1998 altered P dynamics and affected the $\delta^{15}N$ of both NO_3^- and seston. Recent increases in sediment $\delta^{15}N$ in eastern Lake Ontario (Hodell and Schelske 1998) may also be linked to climate warming. In Grand Traverse Bay, we observed higher $\delta^{15}N$ values for seston during a warm year with a relatively long stratified period. If the high seston $\delta^{15}N$ values we observed are mirrored in sinking POM data and consequently in recent sediments, then the increasing $\delta^{15}N$ of sediment may be the indirect result of changing phytoplankton nutrient preferences as a consequence of climate warming.

Synthesis: Conceptual model of the factors affecting the $\delta^{15}N$ of NO_3^- in Grand Traverse Bay

A conceptual model was devised to explain the apparent relationship between the $\delta^{15}N$ of seston and that of NO_3^- which relates the isotopic composition of NO_3^- to its sources via nitrification (Figure 10). Seston and sinking POM are the ultimate sources of NO_3^- in the water column via mineralization and subsequent nitrification (represented by arrows marked *a* in Figure 10). Although NO_3^- inputs from sediment were likely unimportant in this system (Gardner *et al.* 1987), rates of N mineralization and denitrification were not measured. Therefore, a source of NO_3^- originating in the sediments of the bay (represented by arrows marked *b* in Figure 10) cannot be completely discounted. Isotopic fractionation during uptake did not appreciably affect the $\delta^{15}N$ of NO_3^- in Grand Traverse Bay, so fractionation due to uptake (indicated by arrows marked *c* in Figure 10) is considered to be negligible. External N sources and possible inputs from N fixation were not likely to be significant, as discussed previously, and were not included in the model. Thus, the major internal sources of NO_3^- to Grand Traverse Bay may be limited only to seston and sinking POM via remineralization and nitrification. A preliminary average $\delta^{15}N$ value of 10.3‰ for sinking POM (N. Ostrom, unpublished data) agrees well with recent sinking POM isotopic data from Lake Ontario (Hodell and Schelske 1998). The relative contributions of seston and sinking POM to the NO_3^- pool and isotopic fractionation that may be associated with the processes of remineralization and nitrification (indicated by α in Figure 10) have yet to be determined in the bay.

Organic N from seston and potentially from sinking POM, however, contributes to and influences the isotopic signature of NO_3^- in Grand Traverse Bay.

During most of the 1997 sampling season, the $\delta^{15}N$ of seston differed from that of NO_3^- by 3‰ or less. No significant seasonal trend in the $\delta^{15}N$ of NO_3^- was observed (α = 0.05, n = 6) and a relationship between the isotopic composition of seston and that of NO_3^- could not be easily described. The weak relationship between the $\delta^{15}N$ of NO_3^- and that of seston is indicated by the homogenous color of the NO_3^- reservoir at the top of Figure 10. However, the $\delta^{15}N$ of seston at station GT3 was much higher overall in 1998 (avg. = 12.2‰, n = 32) than in 1997 (avg. = 5.6‰, n = 32), likely because of increased ^{15}N-enriched NH_4^+ uptake by phytoplankton in 1998. When organic N from this ^{15}N-enriched seston was remineralized and nitrified, the high isotopic composition of seston was transferred into the NO_3^- pool. As a result, a striking seasonal trend in the $\delta^{15}N$ of NO_3^- was observed in 1998, coupled with a significant relationship between the isotopic compositions of seston and NO_3^- (α = 0.05, r^2 = 0.87, n = 7). The strong relationship between the $\delta^{15}N$ of NO_3^- and that of seston in 1998 is indicated by the strong gradation from dark gray (high $\delta^{15}N$) to light gray (low $\delta^{15}N$) in the NO_3^- reservoir at the bottom of Figure 10. Seston acts as a naturally ^{15}N-enriched tracer in 1998 and allows the qualitative observation of the contribution of seston organic N to the dissolved NO_3^- reservoir in Grand Traverse Bay. In this system, the $\delta^{15}N$ of NO_3^- is dependent upon the isotopic signatures of the reservoirs of organic N contributing to NO_3^- via remineralization and nitrification. Seston is a significant source of regenerated NO_3^- in the bay and therefore, replenishment of NO_3^- in the bay is largely dependent upon internal

processes instead of external N sources. The fact that the $\delta^{15}N$ of NO_3^-, the largest available pool of N in this system, exhibits seasonal variation in 1998 is evidence that internal NO_3^- regeneration must be rapid in Grand Traverse Bay.

In conclusion, changes in the timing of stratification resulted in less P availability to phytoplankton in Grand Traverse Bay. Although phytoplankton likely assimilated a combination of ^{15}N-enriched NH_4^+ and ^{15}N-depleted NO_3^- throughout both 1997 and 1998, isotopic fractionation normally associated with DIN uptake was generally not observed in the NO_3^- pool during either sampling season. Changes in SRP availability during the 1998 season affected the timing of phytoplankton reliance on NH_4^+ as opposed to NO_3^-, and this shift was reflected in higher $\delta^{15}N$ values for seston. The alterations that occurred in Grand Traverse Bay between 1997 and 1998 serve as an illustration of how $\delta^{15}N$ at the base of a foodweb may be affected by longer stratified periods as a result of climate warming. At this time, inputs from processes such as N fixation are not observed, and the replenishment of NO_3^- in Grand Traverse Bay is dependent upon rapid internal regeneration via mineralization and nitrification of organic N from seston and potentially from sinking POM. Long-term changes in the timing of stratification, nutrient chemistry, or external source inputs as a result of climate change, however, may permanently shift phytoplankton populations in favor of those species adept at utilizing low concentrations of nutrients such as NH_4^+ and P. Thus, long-term changes in water chemistry as a result of longer stratified periods may significantly affect nutrients at the base of the food web, and may ultimately change the trophic structure of Grand Traverse Bay.

	Location	Date first ice recorded	Date last ice recorded
1995-1996	East Arm West Arm	02/02/96 02/02/96	04/29/96 04/29/96
1996-1997	East Arm West Arm	01/14/97 01/17/97	04/15/97 04/15/97
1997-1998	No ice recorded on composite images in East or West Arm		
1998-1999	No ice recorded on composite images in East or West Arm		

Table 1: Dates of ice cover on Grand Traverse Bay, Lake Michigan from the winter of 1996-96 to 1998-99 (data from http://www.natice.noaa.gov/pub/archive/Great_Lakes).

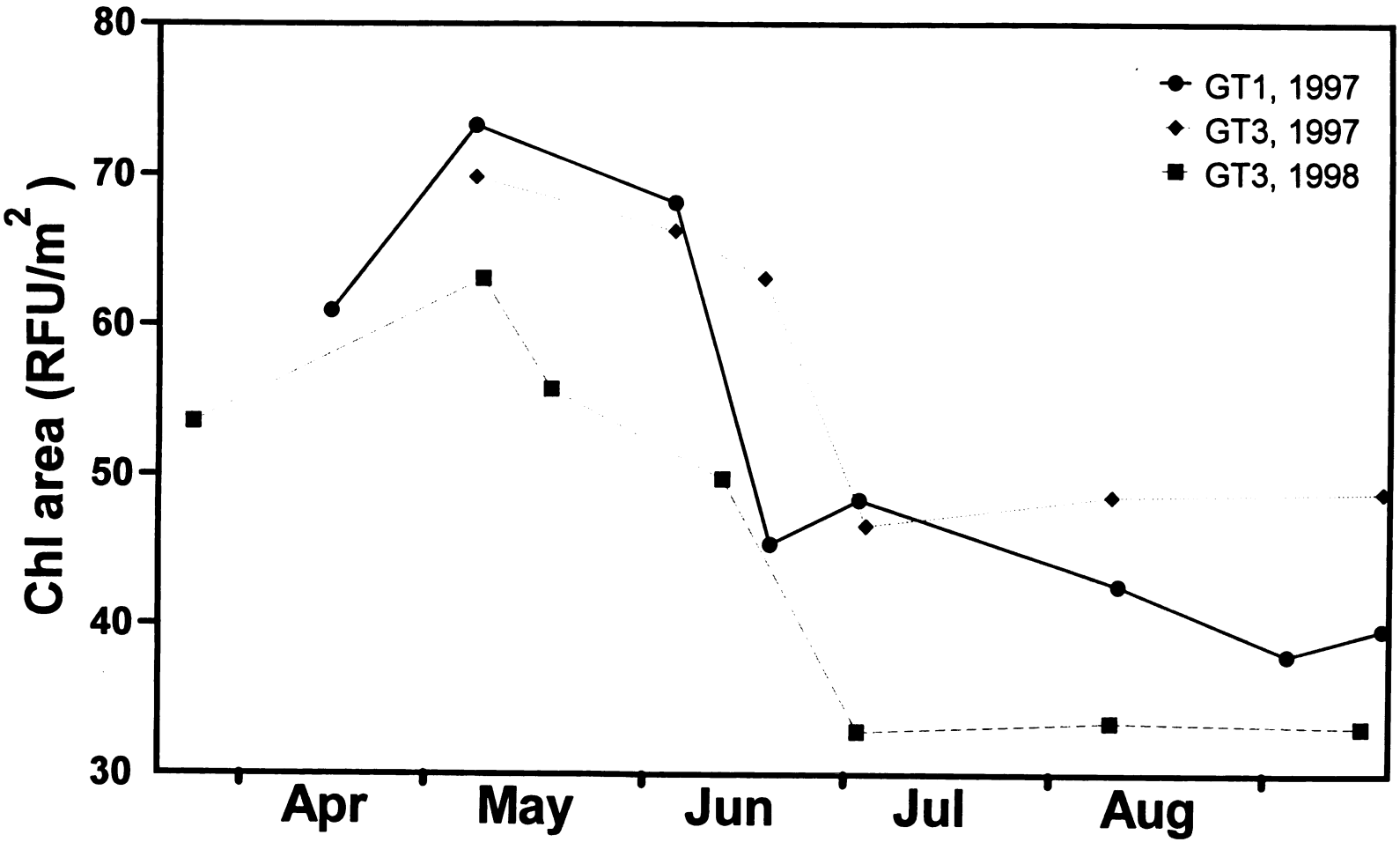


Figure 9: Chlorophyll fluorescence values integrated over the depth of the water column (RFU/m^2) plotted as a function of sampling date for stations GT1 and GT3 in 1997 (from McCusker *et al.* 1999) and for station GT3 in 1998.

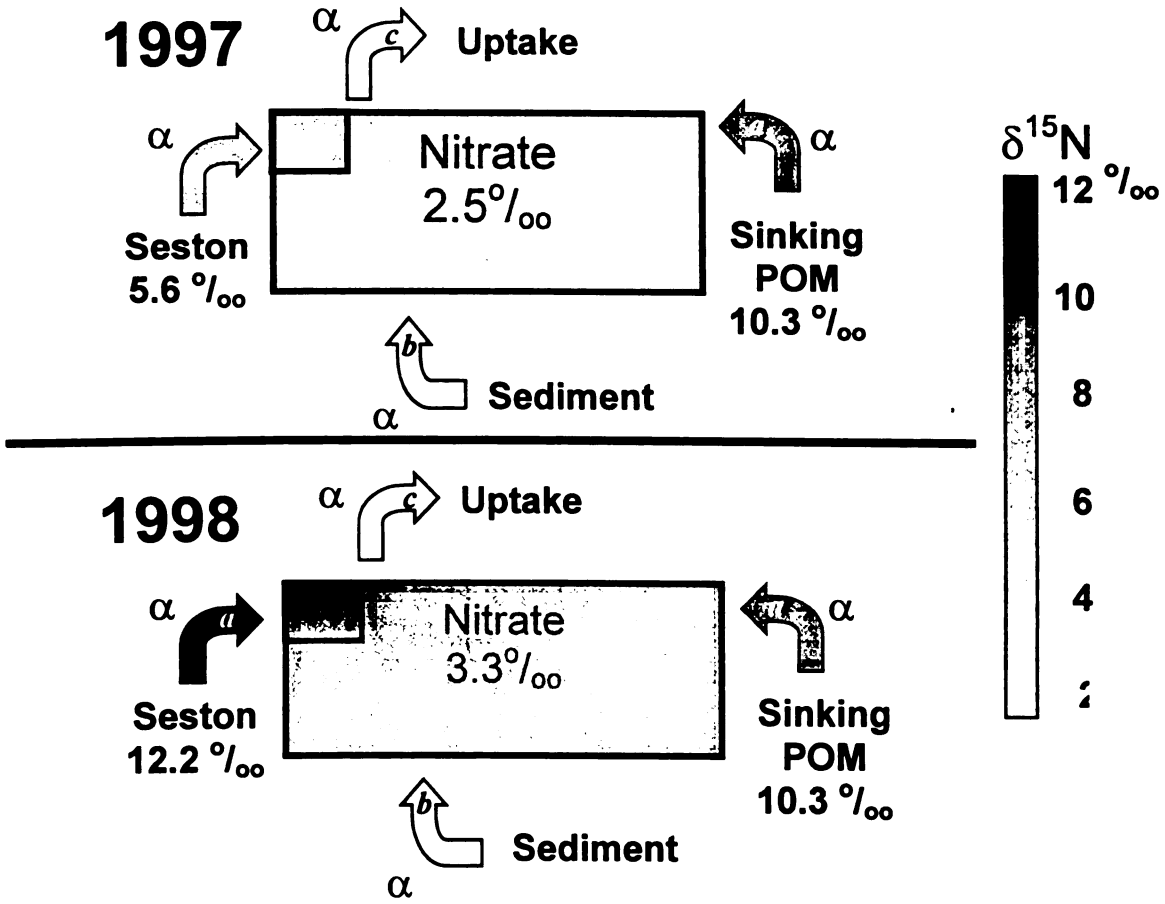


Figure 10: Conceptual model of factors controlling the $\delta^{15}N$ of NO_3^- in Grand Traverse Bay. The $\delta^{15}N$ of NO_3^-, represented by the large shaded box, is affected by inputs from various internal sources (represented by arrows). Inputs from internal sources that appeared to affect the $\delta^{15}N$ of NO_3^- are indicated by shaded arrows with solid borders (*a*), while internal sources or processes whose contributions were not appreciable are shown by unshaded arrows (*b* and *c*). Isotopic fractionation associated with the processes of remineralization, nitrification, and uptake has not yet been determined, or is negligible; the potential for fractionation to occur during these processes is indicated by α. The scale to the right of the figure denotes the $\delta^{15}N$ of all N reservoirs discussed in the model. In 1997, no strong seasonal trends in the $\delta^{15}N$ of NO_3^- were observed (note lack of gradation in 1997 NO_3^- reservoir). In 1998, however, a highly significant relationship was observed between the $\delta^{15}N$ of NO_3^- and that of seston (note strong gradation in 1998 NO_3^- reservoir). The occurrence of ^{15}N-enriched seston in 1998 allowed the qualitative observation of the contribution of seston organic N to the NO_3^- reservoir via remineralization and nitrification.

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