

## Spatial and Temporal Variation of Ammonium in Lake Superior

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**ABSTRACT.** Many aspects of Lake Superior's nitrogen cycle are poorly described in spite of the fact that the lake's nitrate concentration has risen dramatically this past century. One important, yet under-described parameter is the concentration of ammonium. Here, we present data to resolve spatial and temporal variation along with vertical profiles of ammonium concentration in Lake Superior. Lake-wide average concentrations were low ( $0.21 \mu\text{M}$ ,  $n = 166$ ) with considerable spatial and temporal variation. During the onset of summer, the western margin of the lake had higher average concentrations than open and eastern parts. Surface layer ( $<10 \text{ m}$ ) ammonium concentrations showed an increase from January to October. Relatively higher ammonium concentration in the near bottom waters at a number of sites during August indicated efflux from sediment to be an important process. Subsurface maxima near the thermocline were observed in late August and persisted until September-October suggesting that ammonium might be controlled by food web processes during warm, stratified conditions. The higher potential for ammonium uptake compared to external inputs suggested rapid turnover of ammonium in the lake.

**INDEX WORDS:** Lake Superior, ammonium, variation, remineralization, nitrate.

### INTRODUCTION

Lake Superior is one of the largest but least understood lakes in the world. The nitrogen (N) cycle of Lake Superior is of great interest because nitrate has increased almost five fold ( $\sim 5$  to  $25 \mu\text{M}$ ) over the last century (Sterner *et al.* 2007). Most studies attribute this increase to atmospheric deposition of nitrate due to increased N emissions (Bennett 1986, Ostrom *et al.* 1998). However, very little is known about the dynamics of N within Lake Superior.

Generally, one of the most active and important components of the N cycle of aquatic ecosystems is ammonium. Despite low ambient concentrations in many water bodies, ammonium can still be a major source of N for autotrophs and microbes. For example, in the oceans, it accounts for almost 30–90% of the N used by phytoplankton (McCarthy *et al.* 1977, Eppley and Peterson 1979).

In spite of low concentrations and rapid cycling rates, broad-scale temporal and spatial variability in ammonium may persist. For example, Weiler

(1978) showed that ammonium concentrations in surface samples of Lake Superior peaked in September. Knowledge of any variation of ammonium in space and time in Lake Superior will help to delineate different sources and pathways of N. Lake Superior is oligotrophic mostly due to cold and dark physical conditions most of the year (Fahnenstiel *et al.* 1990) and low phosphorus and iron concentration (Sterner *et al.* 2004). External input of total phosphorus to the lake is less than 10% of the requirement for reported rates of primary productivity ( $0.16\text{--}0.89 \times 10^{12} \text{ mol C yr}^{-1}$ ; Hecky 2000, Heinen and McManus 2004). This low level of phosphorus and iron may be an important factor in lower N utilization by the phytoplankton despite its abundant availability. Also, preference for ammonium uptake relative to nitrate (Eppley *et al.* 1969, McCarthy and Goldman 1979) and inhibition for nitrate uptake due to presence of ammonium in marine (Eppley *et al.* 1969) as well as fresh water (Prochazkova *et al.* 1970) bodies is well known. To understand the relative importance of different nutrient sources and their importance in regulating the biogeochemical cycling of the lake, it is important to have a thorough knowledge of ambient concen-

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trations. This becomes more relevant in the light of a recent study (Sterner *et al.* 2007) which suggests in-lake oxidation of reduced forms of N to be one of the major sources of increasing nitrate concentration in Lake Superior.

In general, ammonium concentrations in the Laurentian Great Lakes are low. Values of 0.1–1.3  $\mu\text{M}$  for Lake Michigan (Gardner *et al.* 2004) and 0.29–1.07  $\mu\text{M}$  for Lake Erie (Makarewicz *et al.* 2000) have been reported. Low ammonium concentration ( $\sim 0.4 \mu\text{M}$ ) has also been reported for Lake Ontario (Leggett *et al.* 2000). There are very few reports of ammonium concentration in Lake Superior (Weiler 1978, CCIW surveillance reports, Ostrom *et al.* 1998). Ammonium concentrations in range of 0.11–0.33  $\mu\text{M}$  averaged over a year has been reported in Lake Superior for samples collected between 1968–1976 (Weiler 1978). However, most values for ammonium in the Great Lakes suffer from large uncertainty and poor spatial and temporal resolution due to limited sampling frequencies.

Using a recently developed fluorometric technique, we investigated the spatial and temporal variability of ammonium in Lake Superior. In particular, we examined factors that could affect ammonium concentrations with respect to depth and distance from the shore, as well as the seasonal patterns at a number of sites.

## MATERIALS AND METHODS

### Sampling

Samples were collected during nine cruises conducted during 2005 and 2006 onboard the R/V *Blue Heron* and the R/V *Limnos* (Table 1). Henceforth, cruises conducted on the R/V *Blue Heron* will be

referred to as “NILS” and R/V *Limnos* as “Limnos.” Samples were collected from Niskin bottles attached to a CTD rosette. Around 300 mL of lake water was filtered using precombusted (4 h @ 450°C) Whatman GF/F filters for each sample. Glass fiber filters are known to adsorb ammonium from freshwater samples (Eaton and Grant 1979, Holmes *et al.* 1999); therefore filters were first flushed with sufficient sample water (at least 500 mL) to saturate them with ammonium. There are many extraneous sources of ammonium, and the probability of contaminating samples during collection and preservation is high (Holmes *et al.* 1999). Onboard analysis of ammonium was not practical, so samples were stored in tightly capped HDPE bottles, frozen immediately, and transferred from original bottles immediately prior to analysis.

Overall, more than 160 samples were collected and analyzed from throughout the lake (Fig. 1). Multiple geographically distinct stations were occupied during five cruises and other cruises focused on temporal variability at CD-1 (Table 1). One cruise in January 2006 (NILS 9) was carried out to investigate mid-winter conditions. Data for this period in the lake are rare due to harsh climatic conditions. Three rivers draining into Lake Superior (St. Louis, Knife, and Nemadji) were also sampled at river mouths during June–July 2005 to characterize the riverine inputs to the lake.

Temperature profiles indicated that the lake was well-mixed during January ( $\sim 3.5^\circ\text{C}$ ). The lake was stratified during July and August with surface temperature varying between 11.6 to 19.8°C. The thermocline during this period was in the range of 20–40 m at most of the stations. The thermocline during September–October was slightly deeper (40–60 m) at a few stations and the lake started

**TABLE 1.** Cruises and stations. See Figure 1 for location of stations. These cruises are representative of months shown in the third column as most of the stations were covered during those months.

Cruises	Period	Representative Month	Stations Covered
LIMNOS 1	24 May–7 June 05	May	2, 23, 25, 31, 45, 51, 68, 76, 80, 84, 97, 100, 106, 113, 118, 127, 139, 149, 164, 169, 170, 171, 177, 189, 196, 201, 218, 221
NILS 5	20 July–2 July 05	July	CD-1, EL-1, WM, RM, EM
LIMNOS 2	7 Aug–12 Aug 05	August	23, 31, 51, 80, 106, 113
NILS 6	28 Aug–1 Sep 05	August	CD-1, ON-2, EM, PW1, EL-3 EL-1
NILS 7	17–Sep-05	September	CD-1
LIMNOS 3	27 Sep–11 Oct 05	October	2, 23, 31, 51, 68, 80, 100, 106, 113, 139, 196
NILS 8	2 Oct-05	October	CD-1
NILS 9	31 Jan-06	January	CD-1 and STE-D

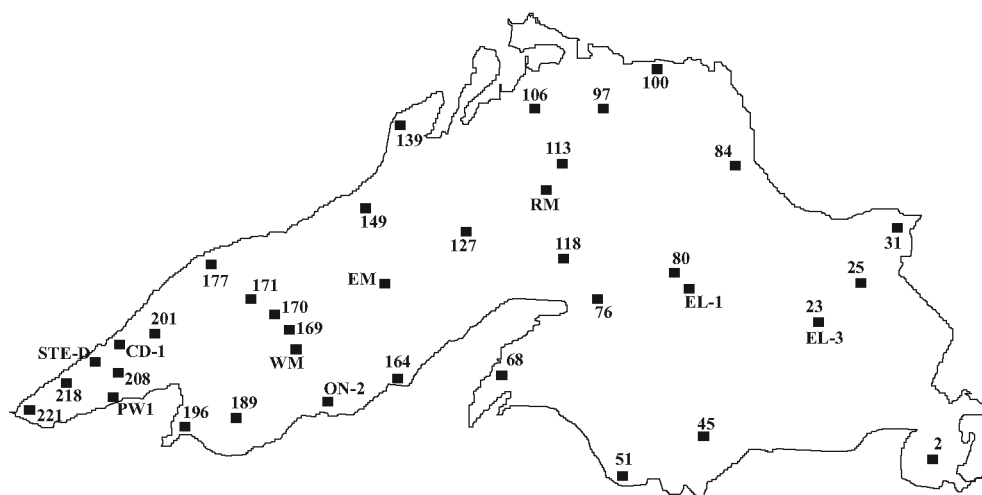


FIG. 1. Location of stations.

showing signs of mixing in the top 10–15 m with surface temperature ranging from 10 to 18.5°C.

### Analysis

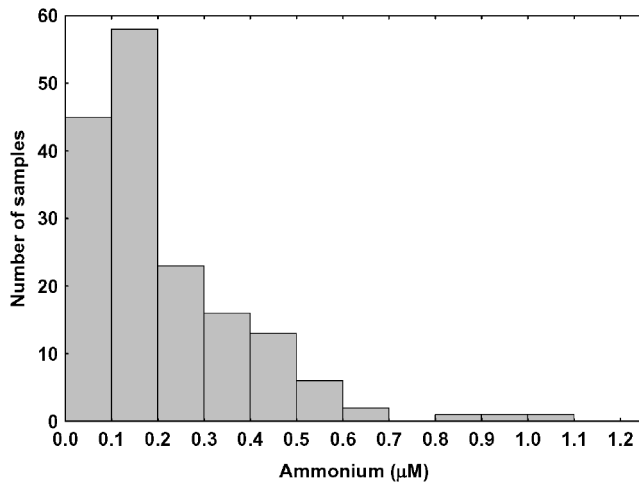
Determination of ammonium in natural systems at submicromolar concentrations has been a difficult analytical challenge. Many methods have been used to measure ammonium in natural waters (e.g., Garside *et al.* 1978, Brzezinski 1987, Gibb *et al.* 1995). The most accurate of all methods so far developed is the fluorometric method (Holmes *et al.* 1999), which is an adaptation of a method proposed by Kerouel and Aminot (1997). The method is based on fluorescence generation due to reaction of ammonium with orthophthaldialdehyde (OPA) in presence of sodium sulphite (Kerouel and Aminot 1997). During the present study, we used protocol A from Holmes *et al.* (1999) with slight modification in volume (20 mL instead of 80 mL). A sample to working reagent ratio of 4:1 was maintained as in the original protocol. The analytical equipment we used was a Turner Designs 10-AU field Fluorometer with optical kit number 10-303. Background fluorescence (BF) was estimated in each sample by adding 5 mL of borate buffer into 20 mL of sample. The value of BF was subtracted from observed sample fluorescence (Holmes *et al.* 1999). BF was always less than 1% of observed sample fluorescence for lake samples whereas it was higher for river samples (< 20% of sample fluorescence). The blanks were always less than half of the fluorescence for lowest standard. The test tubes were cleaned by treating them with working reagent, and

were stored with 5 mL of this reagent. Standards were filled with 20 mL of fresh nanopure water and sample tubes were filled with 20 mL of sample water. The tubes were spiked with ammonium sulfate standard (100–2,000  $\mu\text{L}$  of 10  $\mu\text{M}$  solution). Working in the dark, 5 mL of working reagent was then added to all tubes. Tubes were mixed thoroughly and incubated in the dark at room temperature for 18 h. The precision obtained by this method was remarkable. For example, mean  $\pm$  standard deviation for 15 m water sample from CD-1 ( $n = 3$ ) was  $0.13 \pm 0.006 \mu\text{M}$ . This level of precision was routine.

For chlorophyll *a*, around 200 mL of lake water was filtered in triplicate on 25 mm cellulose nitrate filters and immediately frozen until analysis. Chlorophyll *a* was determined using standard fluorometric method involving 90% acetone extraction (Welschmeyer 1994).

### RESULTS

The ammonium concentrations in Lake Superior were low and variable (range: 0.02–1.05  $\mu\text{M}$ , mean: 0.21  $\mu\text{M}$ , median: 0.16  $\mu\text{M}$ ,  $n = 166$ ). The frequency distribution was left-skewed, with 60% of observations < 0.2  $\mu\text{M}$  (Fig. 2). The lake-wide mean value observed during the present study was within the range observed by Weiler (1978). This suggests that the ammonium concentration in Lake Superior appears not to have changed despite 10–20% increase in nitrate concentration since Weiler's measurements. Despite these low concentrations and the known dynamic nature of ammo-



**FIG. 2.** A histogram showing ammonium data (lake) collected during this study.

nium in freshwaters, consistent variations in space and time were observed.

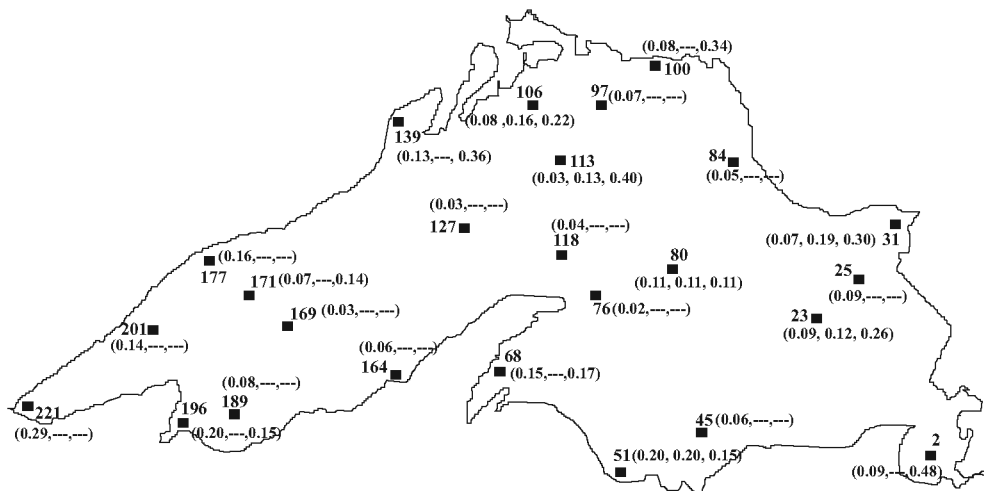
#### Spatial Variation in Surface Layer

Only very limited information on spatial variation in ammonium in Lake Superior has been published before. Weiler (1978) indicated higher concentrations in the far western and far eastern zones. We found a surface layer (< 10 m) average ammonium concentration of around 0.17  $\mu\text{M}$ , close to the lake-wide average of 0.21  $\mu\text{M}$ . The most comprehensive lake-wide surface sampling ( $n = 28$ ) was performed during the May *Limnos* cruise, when

ammonium concentration appeared to be higher in the western half of the lake, particularly close to shore. Six out of eight stations with ammonium concentration > 0.1  $\mu\text{M}$  were very close to the western margin of the lake (Stations 139, 177, 201, 221, 196, and 68; Fig. 3). Average ammonium concentration for stations close to the western margin (mean: 0.14  $\mu\text{M}$ ,  $n = 9$ ) was significantly higher ( $p = 0.004$ ) than eastern and open stations (mean: 0.07  $\mu\text{M}$ ,  $n = 16$ ). Ammonium concentration dropped rapidly with only a few kilometers distance from the shore. For example, Station 189 (0.08  $\mu\text{M}$ ) and 45 (0.06  $\mu\text{M}$ ) were only a few kilometers north from stations 196 (0.20  $\mu\text{M}$ ) and 51 (0.20  $\mu\text{M}$ ) respectively, but sharp declines in ammonium concentrations were seen.

#### Temporal Variation

Previously, Weiler (1978) indicated that surface concentrations of ammonium reached a seasonal peak in September and October. Similarly, we found that surface concentrations during winter months were lower compared to summer months. The average surface layer (< 10 m) ammonium concentration increased from May (0.09  $\mu\text{M}$ ,  $n = 28$ ) to October (0.25  $\mu\text{M}$ ,  $n = 13$ ) and dropped to 0.08  $\mu\text{M}$  ( $n = 2$ ) by January (Fig. 4A). In addition, an ammonium concentration of 0.39  $\mu\text{M}$  was observed at CD-1 during September, the only station sampled during that month. This data point was consistent with the observed temporal trend but is not included in Figure 4A due to lack of samples from



**FIG. 3.** Ammonium concentration observed during May (first in the parentheses), August (second in the parentheses), and October (third in the parentheses). Dashes: not collected at a particular station during that season.

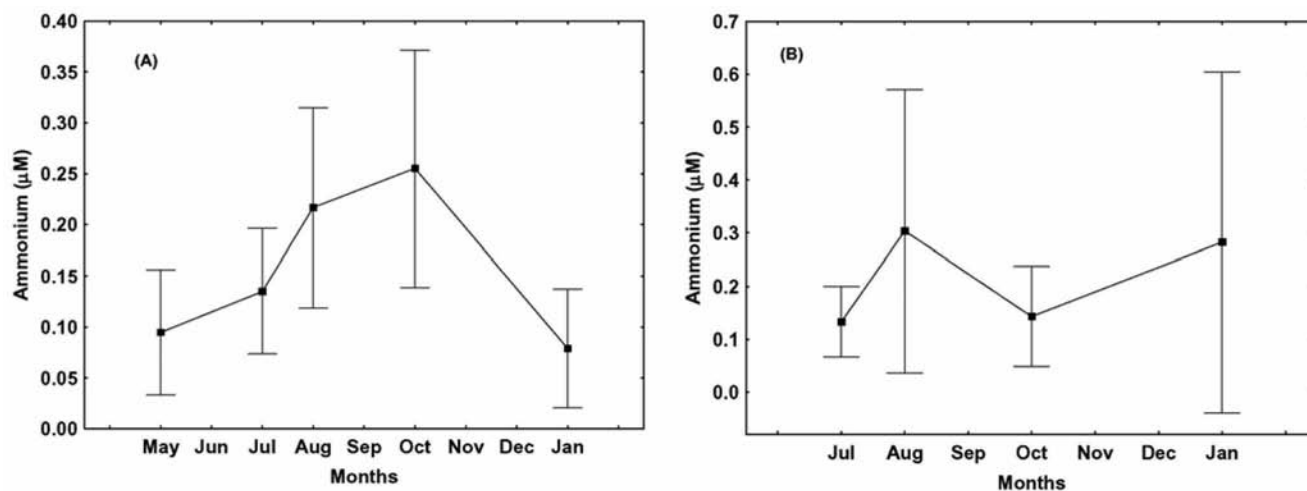


FIG. 4. Average monthly concentration of ammonium in (A) the surface layer, and (B) near the bottom (< 4 m). Vertical bars are standard deviations.

multiple sites. The observed temporal trend did not change and remained significant ( $p = 0.001$ ) even after excluding near shore stations (all stations nearer than Stn.189 from shore). The trend of increasing ammonium from spring to fall was also observed in surface concentration at a larger number of sites for the *Limnos* sites sampled in May, August, and October. More than half of the stations where data are available for all 3 months showed an increase of more than  $0.14 \mu\text{M}$  from May–June to October (Fig. 3). At southern shore station 51 concentrations remained very similar whereas it was temporally stable at a mid-lake station 80 (Fig. 3). This seasonal pattern in surface ammonium concentration appears to be a very robust feature of the lake.

There have been very few measurements of ammonium concentrations near the bottom of Lake Superior (Ostrom *et al.* 1998) and data published have not previously allowed to a consideration of seasonal patterns, if any. Analysis of samples collected within 4 m of the lake bottom suggested higher concentrations during August and January but there was considerable variability (Fig. 4B) in the data and means were not significantly different ( $p = 0.23$ ). The minimum concentration was observed at CD-1 during September ( $0.07 \mu\text{M}$ ) but this has not been included in Figure 4B due to similar reason stated earlier.

#### Vertical Profiles

Similarly, very few vertical profiles of ammonium have been reported previously (Ostrom *et al.*

1998). Vertical profiles of ammonium concentration varied greatly through the year. During July, concentrations remained almost constant throughout the water column (Fig. 5A) and did not show much response to the presence of a thermocline (Fig. 5B). In contrast, profiles observed in the eastern and western regions of the lake sampled during August were different from each other. Profiles during the first week of August in the eastern half of the lake (Fig. 5C) did not show any subsurface maxima whereas, prominent subsurface maxima were observed in the western half sampled during late August (Fig. 5E). The absence of subsurface maxima during early August may be due to limited number of samples near the thermocline (Fig. 5D) during these cruises, therefore, it is possible that subsurface maxima did exist but were not detected. Concentrations showed slight drawdown of ammonium in top 20 m and a large increase near the bottom (< 4 m) for two of the stations.

The subsurface maxima observed in the western half of the lake (Fig. 5E) during late August were mostly between 20 and 40 m at all stations except ON-2, which had elevated concentrations at all depths and an erratic profile. The subsurface maxima during these cruises were at a similar depth as the thermocline (Fig. 5F). This trend of subsurface maxima observed during late August remained until September–October (Fig. 5G) when subsurface maxima in ammonium concentrations were also observed, although the profiles were less consistent at this time. The difference in the depth range of subsurface peaks during September–October (40–50

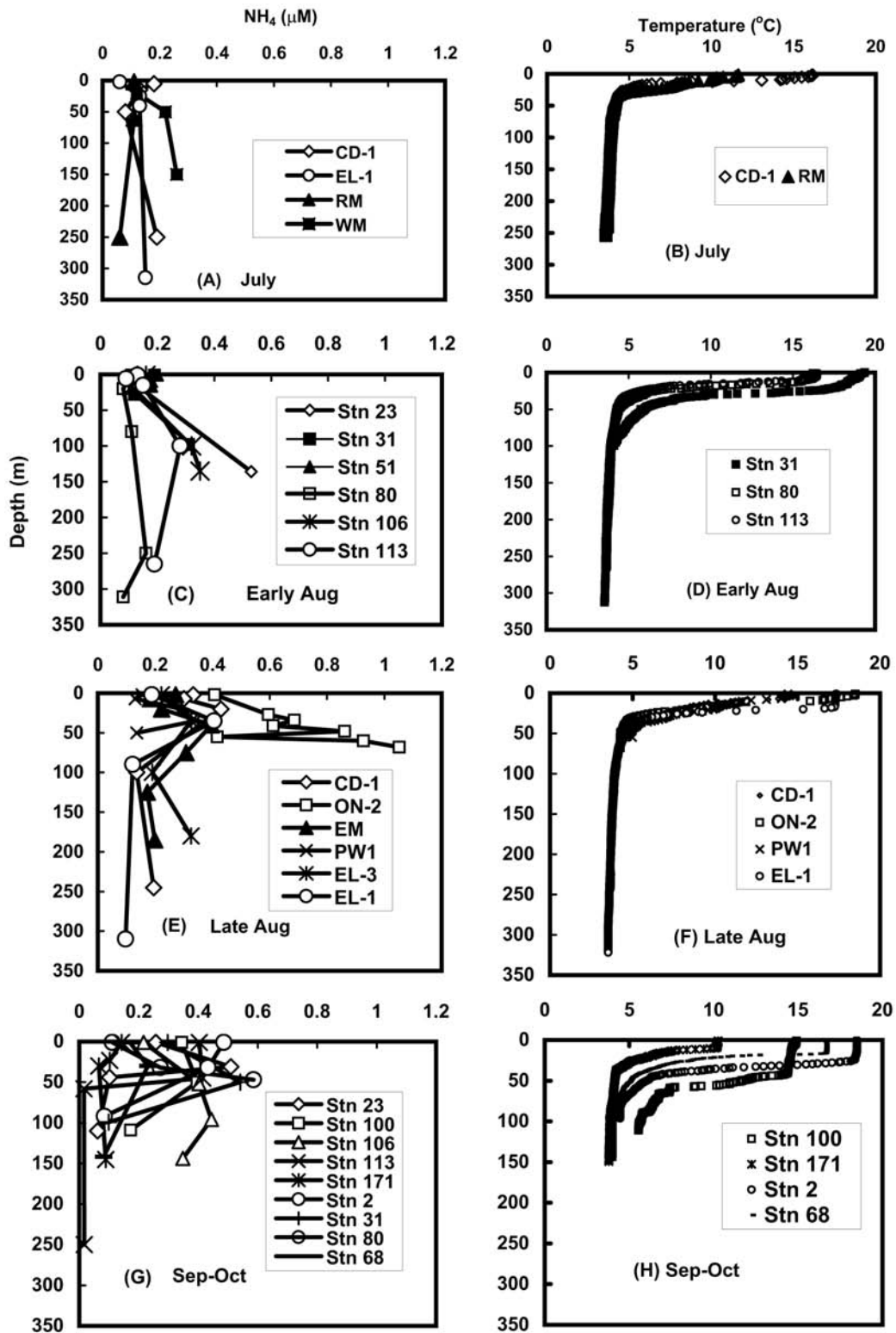


FIG. 5. Vertical profiles of ammonium and temperature during July (A and B), early August (C and D), late August (E and F), and September–October (G and H). Each station was sampled from surface to near bottom (< 4 m from bottom) except station 80 during Sep–Oct 2005, which was sampled only up to 47 m (actual station depth 314 m). Temperature profiles of selected stations only have been shown to maintain the clarity. Temperature profiles for all other stations fell within the range shown in the figure.

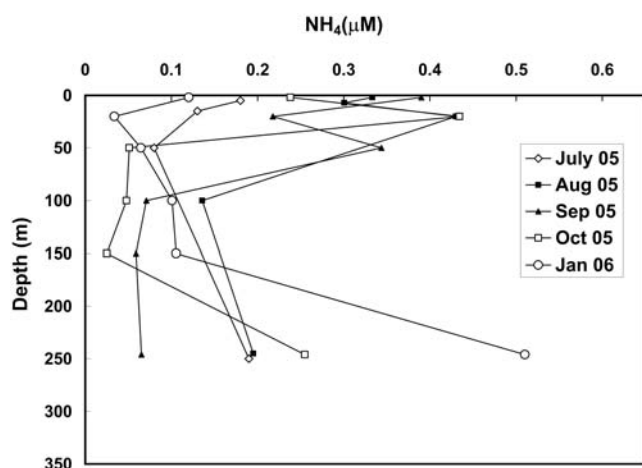


FIG. 6. Month-wise vertical profile of ammonium concentration at CD-1.

m) and late August (20–40m) appears to be consistent with deepening of thermocline during former period (Fig. 5H).

Station CD-1 was occupied most frequently and samples were collected for the whole water column multiple times during the study (Fig. 6). Variations observed at this station showed two important patterns: first, there were subsurface maxima between surface and 50 m for late summer (August, September, and October) with an exception of a minimum at 20 m during September. Values for these 3 months dropped to less than  $0.2 \mu\text{M}$  at 100 and 150 m and again increased at bottom for August and October and remained almost similar during September. Secondly, ammonium concentration during January and July decreased in the first 20 and 50 m respectively and increased toward the bottom similar to August and October. This increase was considerable ( $0.4 \mu\text{M}$ ) during January. In general, variations observed at CD-1 agreed with the profiles discussed earlier.

### Riverine Inputs

Ammonium concentration at the mouths of three rivers draining into Lake Superior: St. Louis, Nemadji, and Knife, were measured. Sampling was performed during June–July 2005. The St. Louis River had the highest concentration ( $1.8 \mu\text{M}$ ) followed by Nemadji ( $0.52 \mu\text{M}$ ). The Knife River mouth had the lowest ammonium concentration ( $0.27 \mu\text{M}$ ), very similar to the average lake value. Higher concentration at St. Louis River mouth might be due to inputs from the nearby city of Duluth, MN. Ammonium concentration measured by

USGS (site 04024000) at St. Louis River (at Scanlon, <http://nwis.waterdata.usgs.gov/usa/nwis/qw-data>) for a long period of time (1972–1994) averages around  $4 \mu\text{M}$ .

### DISCUSSION

Nitrogen in Lake Superior has drawn attention because of a century-long buildup of nitrate (Sterner *et al.* 2007); however, there is still a poor understanding of the N cycle in this lake. Determining the spatial and temporal patterns in ammonium concentration in the lake is a first step in furthering our understanding of the N cycle in Lake Superior.

In general, ammonium in lacustrine environments may be influenced by atmospheric and riverine inputs, gaseous efflux, biological uptake, adsorption to particles, and remineralization (Dodds 1993). Ammonium concentrations in Lake Superior are low, contrasting with elevated and increasing concentrations of nitrate. Spatial and temporal variations of ammonium in Lake Superior suggest different sources and dominance of different biogeochemical processes in space and time in the lake. Though few previous studies have considered spatial and temporal dynamics of the potentially very dynamic ammonium pool in Lake Superior, our study supported previous, earlier studies showing seasonal maxima in late summer, and it indicated for the first time the existence of metalimnetic maxima. It supplements published information on broad-scale horizontal variation in ammonium concentration in the lake.

The geographical location of Lake Superior suggests that inputs from the largely forested and sparsely populated watershed play a limited role. Based on the patterns we observed, it appears that remineralization and recycling may play a major role. Though we did not study rates of remineralization, our observations of the temporal trends and patterns with depth are consistent with important sources of ammonium in Lake Superior being protozoan and zooplankton excretion and remineralization of organic matter in the water column. Elevated ammonium at mid-depth in late summer corresponds to locations of relatively high algal biomass, suggesting enhanced grazing and consumption and therefore also excretion. At most sites during August and September, ammonium in the water column appears to follow the chlorophyll profile (Fig. 7), although increases in ammonium are less than increases in chlorophyll. Similarly, elevated ammonium in nearshore regions is consis-

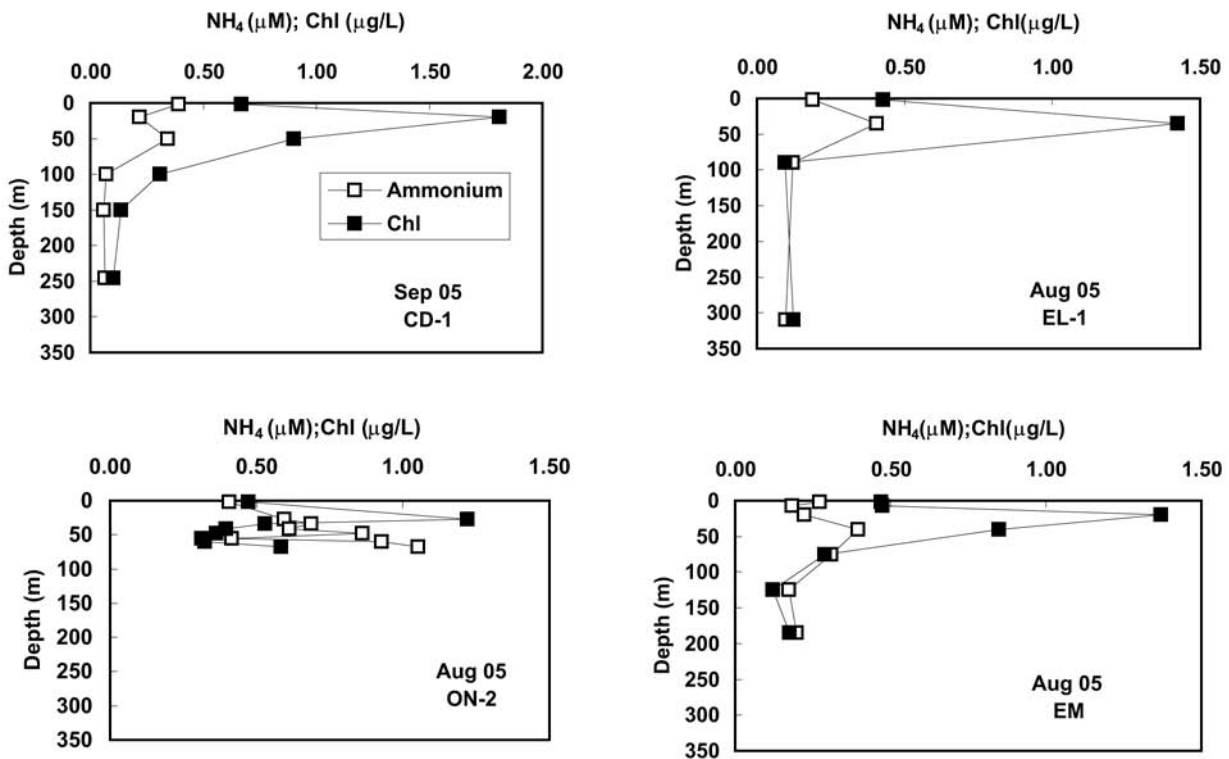


FIG. 7. A few typical profiles showing ammonium and chlorophyll variations with depth during present study. Stations and months of sampling are shown in respective figures.

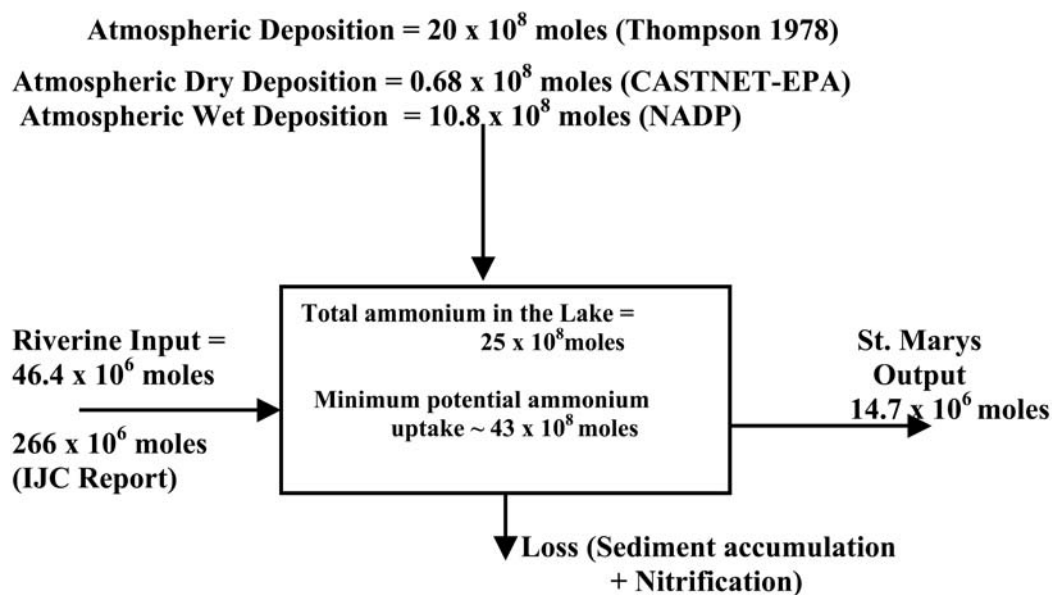
tent with restricted inshore localization of a few zooplankton species in the early spring, and increase in number of species and areal extent during summer and early fall (Watson and Wilson 1978).

The observed vertical profiles during early and late August (Figs. 5C and 5E) suggest the presence of an active sedimentary supply of ammonium to the water column. Relatively high ammonium concentrations in the hypolimnion were often observed, particularly near bottom.

The spatial and temporal pattern observed during the present study has also been observed in other Great Lakes. Similar to St. Louis River mouth during present study, Gardner *et al.* (2004) observed significantly higher ammonium concentration ( $\sim 4.3 \mu\text{M}$ ) near the St. Joseph River mouth in Lake Michigan compared to the open lake ( $0.1\text{--}1.0 \mu\text{M}$ ). This indicates that higher ammonium concentration at nearshore locations in the Great Lakes might be due to some contribution from riverine inputs. Higher ammonium concentration during warmer than cooler period has also been observed in Lake Michigan (Gardner *et al.* 2004) but only in eastern part of Lake Erie (Makarewicz *et al.* 2000). Rela-

tively higher regeneration rates during June compared to March in Lake Michigan (Gardner *et al.* 2004) is in agreement with higher ammonium concentration during former period ( $0.40 \mu\text{M}$  compared to  $0.27 \mu\text{M}$ ). Higher ammonium concentration observed in Lake Superior during summer months may also be due to regeneration or remineralization but as mentioned earlier, regeneration rates remain to be quantified in Lake Superior.

Normally ammonium does not accumulate in the water column of large water bodies because it is taken up by bacteria and phytoplankton following remineralization or excretion. The uptake rates of DIN ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) and their relative preference are not known in Lake Superior. Preliminary results from a related study (Kumar *et al.* In prep.) indicate preference for ammonium in Lake Superior compared to nitrate despite average nitrate concentration ( $\sim 25 \mu\text{M}$ ) of almost 125 times higher than that of ammonium ( $0.21 \mu\text{M}$ ). The reason for this difference may be energy requirements or suppression of nitrate uptake due to presence of ammonium. No clear relationship was found between nitrate and ammonium concentrations which might be because



**FIG. 8.** Major inputs and outputs of ammonium in Lake Superior.

ammonium was much more readily taken up than nitrate.

To understand the ammonium dynamics of the lake on an annual scale, we constructed a lake-wide budget (Fig. 8). Based on the present study (mean concentration:  $0.21 \mu\text{M}$ ), total ammonium in the lake is around  $25 \times 10^8$  moles and annual flux out of Lake Superior through the St. Marys River is around  $14.7 \times 10^6$  moles. The total annual wet deposition of ammonium based on data for four NADP sites near the lake is around  $10.8 \times 10^8$  moles (<http://nadp.sws.uiuc.edu>). Based on EPA clean air status and trends network (CASTNET) site nearest to the lake (Voyageurs NP), annual dry deposition of ammonium is around  $0.68 \times 10^8$  moles (<http://www.epa.gov/castnet/site.html>). A higher estimate of  $20 \times 10^8$  moles  $\text{y}^{-1}$  for ammonium deposition has also been reported (Thompson 1978). One of the most poorly constrained parameters in Lake Superior's ammonium budget is riverine input. Based on average value observed at river's mouth during the present study ( $0.86 \mu\text{M}$ ), the total annual riverine input is  $46.4 \times 10^6$  moles. According to the International Joint Commission (1979), the total riverine ammonium contribution is around  $266 \times 10^6$  moles. Both estimates are much less than the lake's inventory of ammonium.

We calculated potential ammonium uptake rates based on average primary productivity data ( $\sim 65 \text{ gC m}^{-2} \text{ y}^{-1}$ ; Hecky 2000). We used a range of possible C: N ratios (e.g., 10.2, 6.6 and 4.4) to convert

C into N-uptake and assumed different contribution of ammonium uptake (70, 50, 20, and 10%) to total N-uptake. Based on these combinations, minimum and maximum annual ammonium uptake was  $43 \times 10^8$  and  $707 \times 10^8$  moles respectively, substantially higher compared to external inputs and the lake inventory. The high ammonium demand relative to availability suggests rapid turnover of ammonium in Lake Superior waters. Once the ammonium is incorporated into phytoplankton and bacteria in the lake, it is recycled due to biological activity, buried in sediments through organic matter deposition, or converted to nitrate via nitrification in the lake.

At present, N transformations in the lake are poorly known and need quantification. In particular, nitrification has the potential to significantly affect the ammonium concentration of the lake. Lake Superior is well oxygenated and this could favor nitrification. Unfortunately there is no direct estimate of nitrification rates available for Lake Superior, and the abundance and type of nitrifying bacteria are poorly known. There is indirect evidence of nitrification at sediment-water boundary with annual efflux of  $44\text{--}20 \times 10^8$  moles of nitrate per year (Heinen and McManus 2004), which in turn may require significant amount of ammonium to be nitrified. DON may also contribute significantly. A related study indicated that in-lake nitrification contributes virtually all of the nitrate accumulating in the lake (Finlay *et al.* 2007), suggesting an impor-

tant role for nitrification to the N cycle of Lake Superior.

Other processes involved in ammonium cycling appear to be of minor importance in Lake Superior. The recently discovered process known as anammox (anaerobic oxidation of ammonium) is a newly recognized process in the nitrogen biogeochemical cycle where bacteria are known to oxidize ammonium in anaerobic environment (Kuypers *et al.* 2003). However, it is unlikely to be significant in Lake Superior due to the well oxygenated water column. Other processes which may affect ammonium concentration of the lake are volatilization and adsorption. Ammonium volatilization is mostly dependent upon the pH conditions of the lake and is enhanced at elevated pH (Hargreaves 1998). It is quite possible that some amount of ammonium might be escaping from Lake Superior during late summer and early fall when pH is highest. However, in most cases this process is considered to be trivial as a means of nitrogen removal.

### CONCLUSION

Overall, this study presents data on spatial and temporal variation of ammonium in Lake Superior, and provides some preliminary insights into the processes controlling this variation. Ammonium concentrations are low in Lake Superior, as in most of oxic oligotrophic systems, and indicate rapid uptake of remineralized N. Higher ammonium concentration near sediments and subsurface maxima near thermocline support the view that ammonium concentrations in Lake Superior are controlled by biogeochemical processes such as sedimentary and water column regeneration. Some important remaining aspects to be addressed for a comprehensive understanding of ammonium dynamics in the lake include quantification of riverine inputs using more accurate methods than used previously and especially an extensive consideration of biogeochemical process rates. Riverine inputs measured using older techniques may have overestimated ammonium inputs to the lake whereas the rates of ammonium production via biological remineralization or excretion or loss via nitrification are not known for Lake Superior.

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