# Do phytoplankton use more $NH_4^+$ or $NO_3^-$?


## Joanna K. York*[1], Ivan Valiela[1], Daniel J. Repeta[2]

[1] Boston University Marine Program [2] Woods Hole Oceanographic Institution



**2004 EPA STAR Graduate Fellowship Conference** *Next Generation Scientists—Next Opportunities*


### 1. Do phytoplankton use more $NH_4^+$ or $NO_3^-$?

Eutrophication is increasing worldwide and usually begins with increased availability of N to primary producers, primarily as $NO_3^-$.

- Leads to algal & phytoplankton growth
- Causes eelgrass die-off which leads to loss of fin- and shellfish habitat.
- Decomposition of algae leads to hypoxia/ anoxia which may kill organisms that cannot escape.
- Phytoplankton require N as:
  - nitrate ($NO_3^-$)
  - **ammonium ($NH_4^+$) PREFERRED**
  - nitrite ($NO_2^-$)
  - dissolved organic nitrogen (DON)

### 2. Site

Childs River is a sub-estuary of the Waquoit Bay system, on Cape Cod, MA. Land-use on the watershed of Childs River includes a large proportion of residential area, as well as other land-cover types, resulting in a land- derived N-load to the estuary more than 20 times the load to a comparable pristine system.

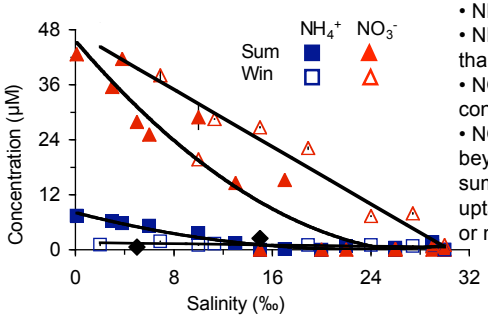
### 3. Methods

We measured concentrations and $\delta^{15}N$ of $NH_4^+$, $NO_3^-$, and chlorophyll *a*. We compared the $\delta^{15}N$ of chlorophyll *a*, $NH_4^+$ and $NO_3^-$ to determine which form of N was used.

Stable Isotopes:

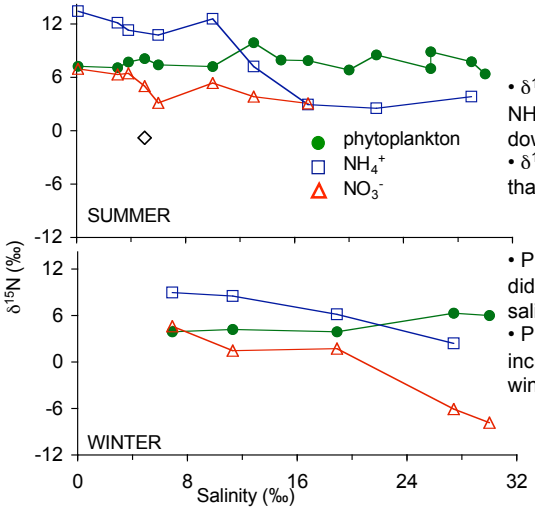
- Ratio of $^{14}N$ and $^{15}N$ varies in different materials
- $\delta^{15}N=[(R_{sample}/R_{standard})-1]X1000$, $R=^{15}N/^{14}N$ (‰)
- Fractionation ($\varepsilon$) is a change in $\delta^{15}N$ during biological reactions because $^{14}N$ reacts faster than $^{15}N$.
- Phytoplankton take up $^{14}NO_3^-$ or $^{14}NH_4^+$ slightly faster than $^{15}NO_3^-$ or $^{15}NH_4^+$; $\varepsilon$ ranges from 4 to 7 ‰ for $NO_3^-$, 0 to 14‰ for $NH_4^+$

### 4. More $NO_3^-$ than $NH_4^+$ was available for phytoplankton




- $NH_4^+ \leq NO_3^-$.
- $NH_4^+$ higher in summer than in winter.
- $NO_3^-$ and $NH_4^+$ behaved conservatively in winter.
- $NO_3^-$ and $NH_4^+$ decreased beyond passive mixing in summer, likely due to uptake by primary producers or microbial processes.

### 5. Phytoplankton acquired their $\delta^{15}N$ from $NH_4^+$ upstream, then maintain $\delta^{15}N$ downstream.

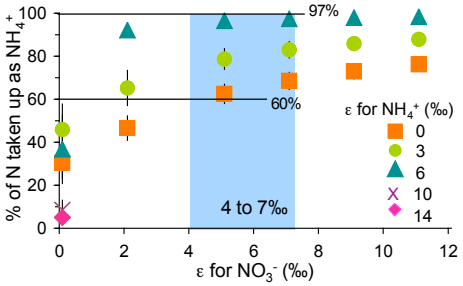



- $\delta^{15}N$ of $NO_3^-$ and $NH_4^+$ decreased down estuary
- $\delta^{15}NH_4^+$ was higher than $\delta^{15}NO_3^-$.
- Phytoplankton $\delta^{15}N$ did not change with salinity.
- Phytoplankton $\delta^{15}N$ increased from winter to summer.

### 6. Phytoplankton in Childs River took up most of their N as $NH_4^+$.

To determine % contribution of $NH_4^+$ and $NO_3^-$ to phytoplankton, we used the following equation:

$$\%NH_4^+ = \frac{(\delta^{15}NO_3^- - \varepsilon_{NO3-}) - \delta^{15}N_{phytoplankton}}{(\delta^{15}NO_3^- - \varepsilon_{NO3-}) - (\delta^{15}NH_4^+ - \varepsilon_{NH4+})}$$




We varied $\varepsilon_{NO3-}$ along the x-axis (0 to 12‰), and $\varepsilon_{NH4+}$ by different symbols (0 to 14‰), and solved the equation using our data for $\delta^{15}N$ of chlorophyll *a*, $NO_3^-$ and $NH_4^+$. The blue shaded area shows solutions for values of $\varepsilon$ for $NO_3^-$ (4 to 7 ‰) and $\varepsilon_{NH4+}$ (0 to 14‰), that are typical of estuarine phytoplankton.

**Childs River phytoplankton derived 60 to 97% of their N from $NH_4^+$.**

### 7. Conclusions

It appears that phytoplankton acquired a significant pool of $NH_4^+$ upstream which provided an N source for growth and division downstream.

Phytoplankton get most of their N from $NH_4^+$, in spite of high $NO_3^-$ in the estuary, so reducing $NO_3^-$ may not solve eutrophication.


* This fellow is sponsored by EPA's STAR or Greater Research Opportunities (GRO) Program.