## Do phytoplankton use more NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup>? Joanna K. York\*<sup>1</sup>, Ivan Valiela<sup>1</sup>, Daniel J. Repeta<sup>2</sup>

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Eutrophication is increasing worldwide and usually begins with increased availability of N to primary producers, primarily as NO<sub>3</sub>.

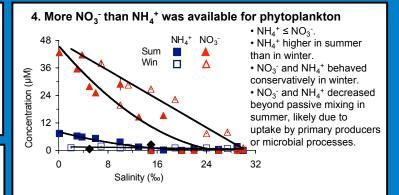
- Leads to algal & phytoplankton growth
- Causes eelgrass die-off which leads to loss of fin- and shellfish habitat.
- Decomposition of algae leads to hypoxia/ anoxia which may kill organisms that cannot escape.
- Phytoplankton require N as:
  - •nitrate (NO<sub>3</sub>-)
- ammonium (NH<sub>4</sub>+) PREFERRED
- •nitrite (NO<sub>2</sub>-) dissolved organic nitrogen (DON)

## 2. Site

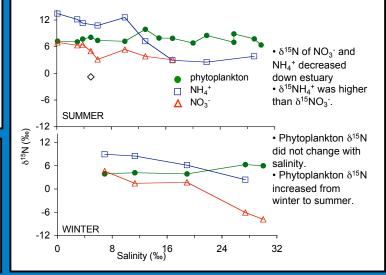
Childs River is a sub-estuary of the Waquoit Bay system, on Cape Cod. MA. Land-use on the watershed of Childs River includes a large proportion of residential area, as well as other landcover types, resulting in a land- derived Nload to the estuary more than 20 times the load to a comparable pristine 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 <sup>14</sup>N and <sup>15</sup>N varies in different materials
- $\delta^{15}$ N=[( $R_{sample}/R_{standard}$ )-1]X1000, R= $^{15}$ N/ $^{14}$ N (%)
- Fractionation ( $\epsilon$ ) 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 $_4^+$ ;  $\epsilon$  ranges from 4 to 7 % for NO $_3^-$ , 0 to 14% for NH $_4^+$



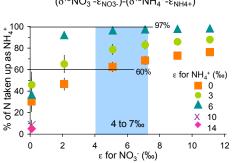
5. Phytoplankton acquired their  $\delta^{15}N$  from  $NH_4^+$  upstream, then maintain  $\delta^{15}N$  downstream.



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

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

$$\% N H_4^{+} = \frac{(\delta^{15} N O_3^{-} - \epsilon_{NO3-}) - \delta^{15} N_{phytoplankton}}{(\delta^{15} N O_3^{-} - \epsilon_{NO3-}) - (\delta^{15} N H_4^{+} - \epsilon_{NH4+})}$$



We varied  $\epsilon_{NO3}$ - along the x-axis (0 to 12‰), and  $\epsilon_{NH4+}$  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  $\epsilon$  for  $NO_3^-$  (4 to 7 ‰) and  $\epsilon_{NH4+}$  (0 to 14‰), that are typical of estuarine phytoplankton.

Childs River phytoplankton derived 60 to 97% of their N from NH<sub>4</sub>+.

**7. Conclusions** It appears that phytoplankton acquired a significant pool of NH<sub>4</sub><sup>+</sup> 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.

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