LONG ISLAND SOUND STUDY FINAL REPORT

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LI 97101301-0, “Natural isotopic tracers for anthropogenic nitrogen in Long Island Sound”

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Public Summary

Anthropogenic nitrogen loading is the common cause of eutrophication in many aquatic systems, particularly in coastal estuaries and embayments. Excess nitrogen over-stimulates biological production leading to reductions in both water column clarity and subsurface oxygenation. Study of natural variations in stable isotopic ratio has repeatedly proven to be a powerful approach for studying biogeochemical cycles especially those for nitrogen and carbon. While past emphasis has been on global scale processes, utility for understanding regional to local anthropogenic impacts is becoming more widely recognized. Almost as a general observation, natural $^{15}N/^{14}N$ ratio ($\delta^{15}N$) has been found to increase with degree of eutrophication over a wide range in aquatic systems. Whether a single mechanism or set of mechanisms is responsible is not known and likely varies with the system considered. Such knowledge, though, is critical to making quantitative use of $\delta^{15}N$ data to diagnose and monitor N-stimulated eutrophication.

In Long Island Sound (LIS), eutrophication has been manifest as seasonal development of hypoxia, particularly at its poorly-flushed western end, during summertime vertical stratification. We have found relatively elevated $\delta^{15}N$ for the entire LIS, correspondingly increasing from east to west by several ‰. Dated sediment cores indicate that the onset of eutrophication and increasing $\delta^{15}N$ began with the urbanization of the LIS watershed in the mid-1800’s. This ^{15}N enrichment could have been caused by 1) higher $\delta^{15}N$ in the anthropogenic N source particularly sewage, 2) biological removal of nitrate in the rivers flowing into LIS, and/or 3) denitrification removal of nitrate in LIS proper under hypoxic conditions. We have conducted a study of the isotopic composition of N sources to LIS as well as a seasonal study of the LIS water column to distinguish between these possible mechanisms.

Denitrification as a generator of high $\delta^{15}N$ values is clearly not as important as originally thought since summertime subsurface O_2 does not appear to become low enough and nitrate concentration not high enough to fuel significant denitrification. Our major conclusions instead include:

1) The high $\delta^{15}N$ values associate with the historical onset of LIS eutrophication are associated with high $\delta^{15}N$ values for sewage N.
2) The dominant anthropogenic source is from WWTP input along the East River.
3) Wintertime accumulation of NO_3^- in LIS is an important phenomenon which preconditions the intensity of the late winter/early spring phytoplankton bloom and likely summertime hypoxia. Winter time NO_3^- increase occurs at a rate almost twice that of WWTP and riverine inputs, most likely from regeneration from the sediments. Significant anthropogenic N has thus been stored in LIS

sediments which may continue to be released back into the water column for some time to come.

Project Period: 1-Jul-2004 to 31-March-2006, extended at no cost to 31-March-2007

Project Description

Eutrophication is the primary cause of the environmental degradation of Long Island Sound (LIS). The seasonal hypoxia it engenders is widely acknowledged as the result of anthropogenic nitrogen (N) and carbon loadings. Quantification of the impact of the anthropogenic N loading on the overall biogeochemical budget for LIS can be substantially improved using natural isotopic tracers (^{15}N/^{14}N, ^{18}O/^{16}O, ^{13}C/^{12}C) as innovative geochemical tools. Prior examination of sediment cores demonstrated increasing δ^{15}N and reduced δ^{13}C with progressive eutrophication beginning in the early 1800's (*pgs. 3 and 4 in accompanying presentation file*). Reduced δ^{13}C is typically the result of increased organic matter degradation in subsurface waters and is used to quantify this effect. However increasing δ^{15}N may have multiple causes. Anthropogenic N from sewage sources is typically enriched in ^{15}N as compared to natural marine sources. Removal of NO_3^- via denitrification under low O_2 conditions would as well lead to increasing δ^{15}N. Fortunately, NO_3^- δ^{18}O can distinguish these influences, only removal processes such as denitrification would lead to parallel increases in δ^{15}N and δ^{18}O in NO_3^- We have carried out a study of the modern LIS to better understand the processes generating these stable isotope effects and to use them to quantify eutrophication-sensitive biogeochemical processes. The combination of seasonally distributed isotopic data for LIS with source signature information for major riverine and sewage treatment plant N sources are being used to address the following <u>questions</u>:

1. What is the relative contribution of anthropogenic vs. natural N sources to <u>central LIS</u>?
2. How important is recycling of N through oxidation of organic matter relative to 'new' N inputs? The effect on N loading with respect to eutrophication and hypoxia is multiplied by the average number of times N is recycled prior to its loss from the system.
3. How important is N loss via denitrification in ameliorating the effect of N loading on the LIS N inventory?
4. Can the sedimentary δ^{15}N record for LIS be quantitatively interpreted with respect to the historical N loading trends and denitrification intensity?

Activities and Accomplishments:

The Ct State DEP database for LIS shows DIN concentrations are low throughout LIS from late winter to early fall but rise to high levels from fall to winter. This made clear to us that a full annual cycle needed to be sampled to document the isotopic signature associated with this important period of high LIS DIN concentrations. High winter NO_3^-concentrations clearly fuel the intense late winter/early spring bloom and determine its isotopic signature. Sediment trap material collected at this time by Dr. Hans Dam have characteristically high δ^{15}N values (*pg. 5 in accompanying presentation file*). Fortunately, the Ct State DEP agreed to collect water samples for us as part of their monthly sampling program which has continued since. This permitted adequate temporal and spatial resolution of LIS sampling for DIN isotopic analysis. Our initial results also showed the importance in identifying East River source isotopic signatures. Thanks to the NYC DEP we have been able to participate in two of their harbor survey cruises to directly sample the East River. We are continuing to collect samples beyond the end of this project in order to identify long-term changes associated with planned WWTP upgrades.

Samples collected to date include major freshwater river inputs to LIS, the East River, as well as LIS proper (*pg. 2 in accompanying presentation file*). The Connecticut, Housatonic, Mattabesset, Farmington, and Salmon rivers have been sampled at 1 to 9 points upriver from their mouths at seven different time periods covering different seasons. Most of the river sampling has been from the Connecticut River since it is the most important riverine source of N to LIS. Sampling of LIS proper has been conducted monthly since April 2005 as part of the regular LIS survey carried out by the CT. State DEP encompassing stations from The Race in the east to the entrance to the East River in the west. At each station a minimum of one near-surface and one near-bottom sample was collected. At a subset of stations, 6-depth profiles were collected for better resolution. In addition, dedicated cruises transecting LIS were conducted in 2004 and August 2005. The East River has also been sampled in Oct. 2006 and Jan. 2007 as a component added in recognition of its likely importance as an isotopic signal source.

Isotopic and chemical analyses are nearly completed for these samples. For water samples, the analytical set includes a) DIC, alkalinity, and DIC $\delta^{13}C$, b) major ion composition, c) NO_3^- $\delta^{15}N$ and $\delta^{18}O$, d) NH_4^+ $\delta^{15}N$. Some water samples have also been analyzed for DON $\delta^{15}N$. Particulate material has been analyzed for N, C_{org}, $\delta^{15}N$, and $\delta^{13}C$.

Summary of Findings

Large variations in $\delta^{15}N$ and $\delta^{18}O$ (NO_3^-) have been observed. River samples show a wide range in $\delta^{15}N$ and $\delta^{18}O$ with co-variation suggesting that much of the range is due to biological processing within the river systems (*pg. 12 in accompanying presentation file*). However, similar $\delta^{15}N$, $\delta^{18}O$ co-variation for WWTP NO_3^- indicates that these inputs are also an important factor. Elevated $\delta^{18}O$ for river samples in April is an indicator for input from atmospheric sources possibly stored over the winter in the watershed and released at this time. Samples from just the river mouths show a narrower range in $\delta^{15}N$ of 5 to 12 ‰ for $\delta^{15}N$ and 0 to 8 ‰ for $\delta^{18}O$ (*pg. 13 in accompanying presentation file*). East River NO_3^- - by contrast has $\delta^{15}N$ values of 4 to 6 ‰ and $\delta^{18}O$ values and 0.5 to 3 ‰. However, when the significant NH_4^+ pool for the East River is factored in, the East River $\delta^{15}N$ signature is 9 to 11‰ (*pgs. 10-12 in accompanying presentation file*). WWTP's that have not been upgraded by N reduction have a similar signal for the $\delta^{15}N$ of the discharged NH_4^+ of 8 to 10 ‰ (NO_3^- discharge in these cases is relatively minor).

Inspection of the seasonal variations in LIS nutrient concentration from the Ct State DEP database shows very low NO_3^- and NH_4^+ throughout LIS during the summer even within the hypoxic zone (*pg. 7 in accompanying presentation file*). Without a NO_3^- pool, there can be no significant water column denitrification and hence no isotopic impact from this process. Denitrification in the sediments is likely occurring but this process is known not to result in a net isotopic signature for the overlying water column. Concluding that elevated $\delta^{15}N$ in LIS is due to source effects alone, we took advantage of the fall/winter increase in LIS NO_3^- to examine isotopic source signals in absence of removal by phytoplankton (*pg. 8 in accompanying presentation file*). NO_3^- accumulating in central LIS between Oct. and Jan. have $\delta^{15}N$ and $\delta^{18}O$ values between 9 and 11‰ and 1 and 4 respectively (*pgs. 9-12 in accompanying presentation file*). The $\delta^{18}O$ for this accumulating NO_3^- is consistent with its production by nitrification in brackish to saltwater. These δ^{15}N values are consistent with sources from sediment N release, input from the East River, and NH_4^+ discharged directly by WWTP that have not been upgraded. A cross-plot of NO_3^- δ^{15}N and δ^{18}O shows that inputs from rivers cannot be contributing significantly to the fall/winter buildup of NO_3^- in LIS (*pg. 13 in accompanying presentation file*).

We had hypothesized that the elevated δ^{15}N signatures in LIS are both the result of isotopically heavy anthropogenic source signatures as well as denitrification processes in LIS. One outcome of this project is that source signatures are dominant. The use of δ^{18}O in NO_3^- data contributed to this finding by permitting us to unravel the relative influence of these two factors. The highest contributions of N are found in western-LIS with a mixing gradient with marine N to the east. Knowledge of the LIS flushing characteristics lead to calculation of total anthropogenic N loading with greater certainty than current estimates. The effects of decreased N loading in the future should be observed by decreases in δ^{15}N, particularly in the western half of LIS. We continue to work toward include a geochemical estimate of anthropogenic N loading to LIS with greater certainty than existing direct measurements (*pg. 15 in accompanying presentation file*). Given a detailed understanding of LIS N isotopic systematics, the history of this loading may be quantified and examined for any evidence for the effectiveness of recent remediation efforts. Lastly, the future effectiveness of remediation can be economically monitored by examining δ^{15}N archives in the form of sediments, bivalves, and water samples collected at a few locations.

Conclusions

Our major conclusions include:

3) The high δ^{15}N values associate with the historical onset of LIS eutrophication are associated with high δ^{15}N values for sewage N. Denitrification in LIS proper is not a cause of high δ^{15}N.
4) The dominant anthropogenic source is from WWTP input along the East River.
5) The wintertime accumulation of NO_3^- in LIS is at a rate almost twice that of WWTP and riverine inputs, most likely from regeneration from the sediments. Significant anthropogenic N has thus been stored in LIS sediments which may continue to be released back into the water column for some time to come.

Presentations/Publications/Outreach

We have presented the results of this project at the last LIS research conference this and at national AGU and ASLO meetings. The most recent presentation was at the summer 2007 ACS meeting in Boston. That presentation accompanies this report. A paper to L&O is currently being prepared as well a book chapter to the planned LIS volume, though a number of additional papers in the peer-reviewed literature are anticipated at this project's close. Related work examining NO_3^- isotopic composition in Ct rivers has been published: Anisfeld, S. C., R. T. Barnes, M. A. Altabet, and T. Wu (2007) Isotopic Apportionment of Atmospheric and Sewage Nitrogen Sources in Two Connecticut Rivers. *Environmental Science & Technology* **41:** 6363-6369

Other

See attached presentation made at the 2007 meeting of the American Chemical Society (Boston)