

## New Tools for Assessing Water Quality: Stable Isotope Analysis of Nutrients

Eutrophication of coastal waters from the excessive input of nutrients is a widespread problem throughout coastal ecosystems. Unlike inputs of toxic chemical contaminants that are generally highest in industrialized urban areas, nutrient inputs occur in both urban and less developed sections of the coast. Nutrients can be derived from point sources, such as effluent discharges, and non-point sources, such as agricultural runoff and residential developments.

In moderation, nutrient inputs can be beneficial: nutrients stimulate phytoplankton production and result in increased fish and shellfish production. Excessive nutrients, however, can result in excessive phytoplankton growth that may result in blooms of nuisance species, low oxygen conditions from decaying algae, or loss of eelgrass or other submerged aquatic vegetation that serve as important habitat for fish and shellfish populations.

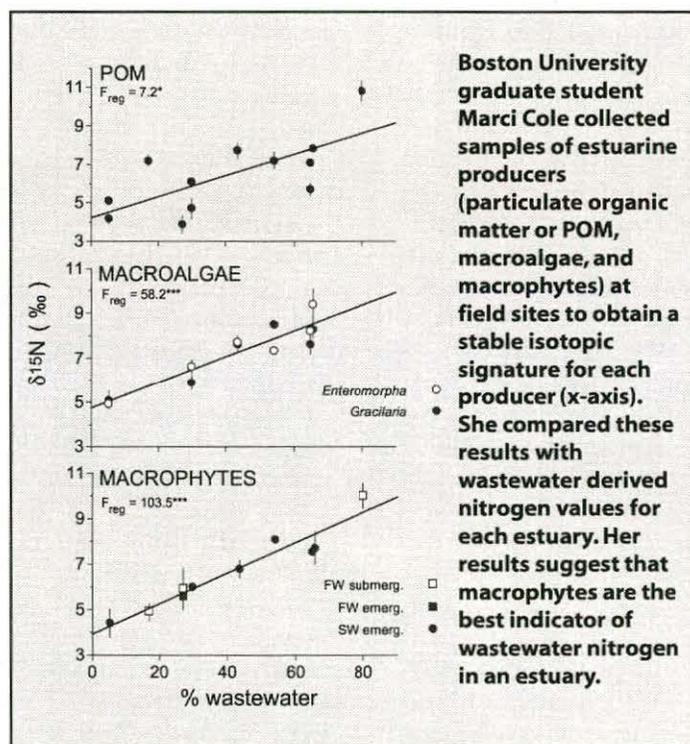
Determining the level of nutrients that have beneficial or detrimental effects on an ecosystem is a challenge that ecologists and environmental managers must address. Having a technique or a set of measurements that would help determine the fate of

waste-derived nutrients in a coastal ecosystem—and the resulting effects on coastal food webs—would greatly enhance our understanding of this problem before extensive and irreversible damage has occurred.

One such technique cur-

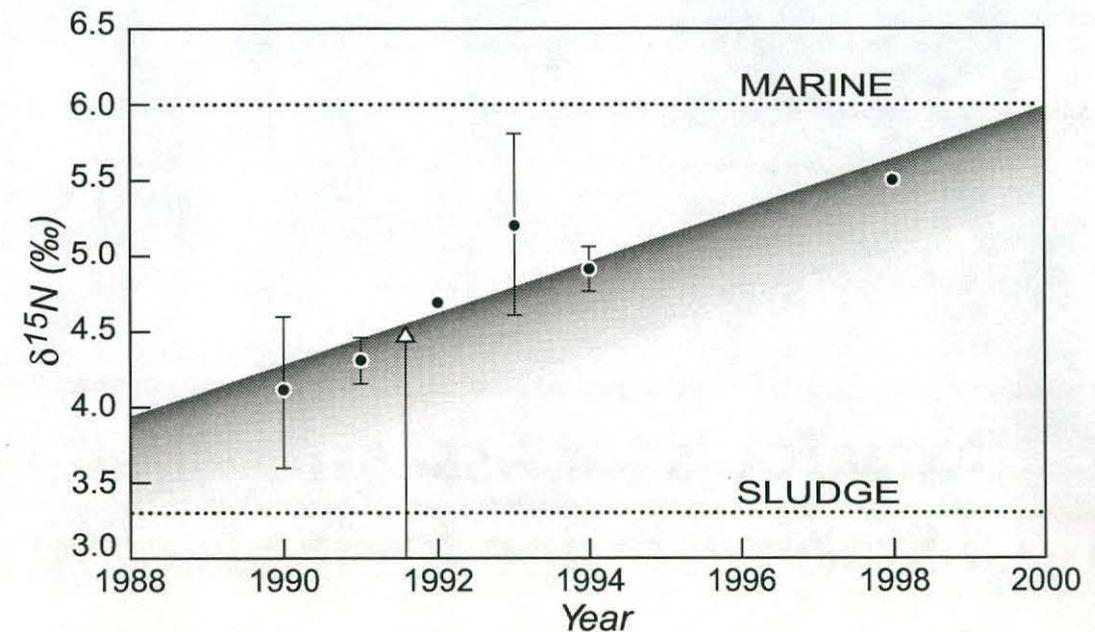
rently used to identify the fate of waste-derived nutrients in coastal embayments is the application of stable isotope analysis of nutrients. Stable isotope analyses have been used extensively during the past decade for identifying food web interactions and biogeochemical processes. The basis of this technique is that the stable isotopic composition of organic matter is based on a few well-characterized reactions. These reactions, in turn, produce isotopic signatures that are generally conserved in food web processes with only minor changes. Thus the stable isotope ratios of a compound can provide information about the reaction responsible for its formation. If an organism's nutrient supply is derived from isotopically discrete sources, the stable isotope ratio of the organism may reflect the importance of each nutrient source.

The use of stable isotopes for examining food web relationships or for tracing



the fate of nutrient sources relies on the assumption that different producers and/or different sources of nutrients have distinct ratios of the naturally occurring isotopes of a particular element. These ratios can be incorporated into a simple two-source mixing model to illustrate the value of using stable isotopes as a way to track nutrient sources. The relative contribution of two sources of nutrients, mixed in a sediment sample or assimilated by an organism, is estimated by calculating the weighted average of the stable isotope signature of the sample in respect to the two sources. When nutrient sources have distinct ranges in stable isotope signatures, the stable isotope signature of the sample reflects the relative contribution from each source.

Such techniques serve as the basis for several WHOI Sea Grant-supported projects aimed at understanding the fate of waste derived nutrients. One project, led by Boston University Marine Program professor, Ivan Valiela, and his former student, James McClelland, used stable isotope ratios of nitrogen to track wastewater from coastal watersheds into estuarine food webs. There are three major sources of nitrogen (N) inputs to estuaries from coastal watersheds: wastewater, atmospheric deposition, and fertilizers—each with a distinct stable isotopic signature. In their study, Valiela and McClelland found that the signature of groundwater-borne wastewater is elevated relative to the other sources of nitrogen. Thus, wastewater acts as a



**This graph shows the change in annual average delta 15 nitrogen ( $\delta^{15}\text{N}$ ) over time for the northern harbor stations in Boston Harbor, Mass. Results indicate a marked reduction in nitrogen derived from sewage sludge since the improvement in wastewater treatment and sludge disposal.**

signature-enriched tracer introduced to estuaries. What's more, these investigators found that, even with low levels of nitrogen loading, elevated levels of the nitrogen ratios can be detected in estuarine plants and animals, thus demonstrating a direct link with wastewater discharges and incorporation into estuarine food webs.

Current Valiela graduate student Marci Cole is extending the McClelland work by conducting a more extensive field sampling program to gather data on nitrogen concentrations for groundwater and wastewater nitrogen signatures in a number of locations, ranging from estuaries to freshwater ponds, to a salt pond.

Cole compared her values to the modeled wastewater nitrogen load for each estuary. Her results show that a relationship exists between the isotopic signal of ground-

water and producers, and the wastewater nitrogen load value derived from the model (see graph, page 1). This relationship can be used to predict what percentage of nitrogen—of all the nitrogen coming into an estuary—is coming from wastewater via groundwater.

Using stable isotope techniques, scientists can now detect the impacts of increased wastewater loading at the molecular level—before changes at the population and community levels. This early detection is critical for making effective land use management decisions in coastal regions.

In a related project, WHOI geochemist Matt Charette is using radium isotopes to look at sub-surface groundwater pathways to embayments in southern New England. These pathways, also known as submarine groundwater discharge

(SGWD), are thought to play a role in delivering nutrients, such as nitrate and phosphate, to coastal waters.

Charette samples for groundwater along the fringes of the embayments and for salinity, dissolved oxygen, depth, pH, and tidal height within the estuaries. He also samples in different seasons and over the course of a tidal cycle.

One study site, the Pamet River estuary in Truro, Mass., yielded surprising results: what was thought to be the least impacted site may be the most impacted. A summer sampling showed a rapid increase in nitrate concentration as the tide went out, over two tidal cycles. This nutrient spike, as it turns out, corresponds with the nitrate concentration in the groundwater. And, with minimal surface runoff to Pamet, these factors seem to implicate groundwater as the pri-

mary source of nitrate.

Charette, along with Valiela graduate student Kevin Kroeger, has just begun work to determine the source of groundwater-borne nitrogen using stable nitrogen isotopes. Likely culprits are wastewater and fertilizer. Those results, coupled with his work in identifying nitrogen trouble spots on a small-scale will be useful to resource managers in coastal areas.

In another WHOI Sea Grant-supported study, investigators at the Marine Biological Laboratory's Ecosystems Center, led by Anne Giblin and Charles Hopkinson, Jr., are using stable isotopes to trace sewage-derived material through Boston Harbor and Massachusetts Bay. This study is complemented by a similar

study led by Joseph Montoya, formerly at Harvard University, with support from MIT Sea Grant. These investigators are part of a multidisciplinary team that is assessing the effects of an ongoing effort to improve waste treatment and change the design and location of effluent discharge from Boston and surrounding communities. These investigators are using stable isotope ratios of nitrogen ( $\delta^{15}\text{N}$ ) and sulfur ( $\delta^{34}\text{S}$ ) to determine the fate of sewage inputs. Sediment samples were analyzed to determine the historical record of sewage inputs including recent changes in treatment and discharge. Plant and animal samples were also analyzed to evaluate the effect of sewage-derived nutrients on local food webs.

Results of these investigators clearly indicate that a large percentage of organic matter in Boston Harbor sediments was derived from the discharge of sewage sludge and effluents: samples taken from other sections of Massachusetts Bay showed only minor contributions of sewage to sediment organic matter, while Boston Harbor sample results reflected a decrease in "sewage" contribution to Boston Harbor after cessation of sludge disposal to the harbor. Food webs at several sites in Boston Harbor and Massachusetts Bay also indicate a "sewage" signal, illustrating that the sewage signal is passed throughout the food web over time (see graph, page 2).

The results of these Sea Grant-supported investiga-

tions are promising indications that the early effects of nutrient enrichment can be traced through watersheds and into food webs. Furthermore, the results of these studies will be important considerations in the development of long-term management actions for small embayments, such as Waquoit Bay on Cape Cod, and harbors, such as Boston Harbor. Information gained by these projects will play an important role in the management of these, and other systems threatened by excessive nutrients, in the future.

For more information about the research profiled in *Focal Points*, contact WHOI Sea Grant at the address shown above.