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Carbon stable isotopes as indicators of coastal eutrophication

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Abstract. Coastal ecologists and managers have frequently used nitrogen stable isotopes ($\delta^{15}N$) to trace and monitor sources of anthropogenic nitrogen (N) in coastal ecosystems. However, the interpretation of $\delta^{15}N$ data can often be challenging, as the isotope values fractionate substantially due to preferential retention and uptake by biota. There is a growing body of evidence that carbon isotopes may be a useful alternative indicator for eutrophication, as they may be sensitive to changes in primary production that result from anthropogenic nutrient inputs. We provide three examples of systems where $\delta^{13}C$ values sensitively track phytoplankton production. First, earlier (1980s) mesocosm work established positive relationships between $\delta^{13}C$ and dissolved inorganic nitrogen and dissolved silica concentrations. Consistent with these findings, a contemporary mesocosm experiment designed to replicate a temperate intertidal salt marsh environment also demonstrated that the system receiving supplementary nutrient additions had higher nutrient concentrations, higher chlorophyll concentrations, and higher $\delta^{13}C$ values. This trend was particularly pronounced during the growing season, with differences less evident during senescence. And finally, these results were replicated in the open waters of Narragansett Bay, Rhode Island, USA, during a spring phytoplankton bloom. These three examples, taken together with the pre-existing body of literature, suggest that, at least in autotrophic, phytoplankton-dominated systems, $\delta^{13}C$ values can be a useful and sensitive indicator of eutrophication.

Key words: carbon; $\delta^{13}C$; estuary; eutrophication; mesocosm experiments; monitoring; Naraganssett Bay, Rhode Island, USA; phytoplankton production; Spartina alterniflora; *stable isotope;* Typhus angustifolia.

INTRODUCTION

One of the major themes in coastal ecology research today is to understand how human sources of nutrients impact coastal ecosystems. In particular, excess amounts of anthropogenically derived nitrogen (N) and phosphorous (P) support excess growth of primary producers (i.e., cultural eutrophication), which can have negative impacts like the proliferation of harmful algal blooms and the development of low-oxygen bottom waters and benthic shading (e.g., Rabalais 2002, Driscoll et al. 2003). Thus there has been great interest in both tracking the sources of nutrients to the coastal zone as well as following how the N and P move through the ecosystem. One popular way to track sources and fate of N (and by association, P) is through the use of the ratio of the stable isotopes of N ($\delta^{15}N$). About 0.4% of the time N will have an extra neutron in its nucleus, causing it to be slightly heavier than the other 99.6% of N atoms (Fry 2006). As both the heavy and light isotopes of N are naturally occurring, and biological and chemical processes typically prefer the light but retain the heavy, ecologists can look at the ratios of heavy-to-light atoms to gain an understanding of where the N comes from and how it moves through a food web. The ratios are expressed in delta notation (δ) where $\delta^{H}X = [(R_{sam} - R_{std})/R_{std}] \times 1000$, X is N or carbon (C), H is the heavy isotope, and R is the ratio of heavy to light isotopes. The differences in δ values, i.e., the heavy : light ratio of a sample relative to a standard, are generally positive for $\delta^{15}N$, but negative for the C isotope, $\delta^{13}C$.

In general, animal sources of N (including sewage) have higher $\delta^{15}N$ values than marine continental shelf sources. For example, N from human sources has $\delta^{15}N$ values that are frequently $>10‰$, whereas isotope values of N from offshore of the continental shelf are typically $<6‰$ enriched (Cabana and Rasmussen 1996, Sheats 2000, Fry 2002, Chaves 2004). Because N in synthetic fertilizers is fixed from the atmosphere, which is also used as a reference standard (by convention, atmospheric N is 0‰), they typically have a $\delta^{15}N$ of $\sim 0‰$ (Fry 2006). By measuring the $\delta^{15}N$ values in dissolved inorganic nitrogen or plant and animal tissues, scientists often can glean information about both the source of the nutrients and the extent of anthropogenic influence (Michener and Kaufman 2007). However, this technique is not without its complications. For example, sewage does not always have high $\delta^{15}N$ values. The $\delta^{15}N$ values in effluent vary with how the waste is treated and the dissolved nutrients are analyzed (ammonium vs. nitrate), as well as with a number of other possible factors (Sheats 2000). During transport from the watershed to the coast, fertilizer $\delta^{15}N$ values are often transformed and can be quite high by the

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