

## Compound-specific nitrogen isotope measurements in ecosystem studies

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The stable isotopes of nitrogen have been widely used in studies of elemental cycling in both terrestrial and aquatic ecosystems. In these studies, the  $\delta^{15}\text{N}$  of organic matter is commonly used as an indicator of the sources of N supporting production as well as an index to the trophic status of organisms within ecosystems. When primary producers as well as consumers are available for analysis, this approach can yield information on both sources and internal processing of N within the ecosystem, but many field programs and paleochemical projects are severely constrained in the number and type of samples available for analysis. This places a high premium on extracting as much information as possible from any available organic sample. In this context, studies of the isotopic composition of individual compounds isolated from organisms or sediments can provide information on the biological processing of nitrogen with a specificity and precision not available with any other technique.

A number of individual biocompounds have been targeted for nitrogen isotopic analysis, including photosynthetic pigments and amino acids. Pigments can provide specific information on the nutrient sources used by primary producers, while amino acids can potentially provide information on both nitrogen sources and the processing of nitrogen within food webs. This additional information is recorded in the differential behavior of individual amino acids: some show large trophic shifts between food and consumer (e.g., glu), while others appear to be conserved during transfer through the food web (e.g., phe). In particular, the difference  $\delta^{15}\text{N}(\text{glu}) - \delta^{15}\text{N}(\text{phe})$  provides a robust index to trophic position in aquatic consumers (McClelland and Montoya 2002). Since  $\delta^{15}\text{N}(\text{phe})$  preserves the  $\delta^{15}\text{N}$  of the primary producers at the base of the food web, isotopic analysis of amino acids also provides an unambiguous index to processes involving primary producers such as  $\text{N}_2$ -fixation (McClelland et al. 2003). Although this approach has not yet been widely used in paleo studies of the nitrogen cycle, the nitrogen isotopic composition of amino acids in preserved organic matter and biomolecules (e.g., chitin) is an obvious target for research into the past dynamics of the nitrogen cycle.

### References

- McClelland, J. W. and J. P. Montoya (2002), *Ecology* **83**, 2173-2180.  
McClelland, J. W., C. M. Holl, et al. (2003), *Deep-Sea Res. In Press*.

## Seasonal speciation of mercury in the Venice lagoon (Italy)

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The Venice lagoon is a large, shallow estuary which was heavily contaminated by Hg cell chlor-alkali plants and other industries located on its western shore. Past studies have investigated problems related to environmental pollution, particularly eutrophication, but no comprehensive research has yet been undertaken to explore the biogeochemistry of Hg. Studies conducted in the 80's and 90's showed 1.20 mg/kg Hg in the sediments near the industrial zone, decreasing to approximately 0.2 mg/kg in the more isolated areas. Recently, mercury was identified as the metal posing the greatest environmental risk, but as yet,  $\text{CH}_3\text{Hg}$  has not been reported for any ecosystem compartment. Since the lagoon harbours extensive salt marshes and contains high  $\text{SO}_4^{2-}$  and nutrients, it is likely to act as a microbiological incubator for Hg methylation.

Here we report the initial findings of a seasonal survey (2001-2003) of Hg and  $\text{CH}_3\text{Hg}$  in the water column, suspended matter, sediments and some selected marine biota samples collected and analysed using ultra-clean techniques. Samples were collected quarterly (from November 2001 to May 2003), mostly from sites in the north-central lagoon, within 10 km of Venice and the Marghera Industrial zone, including urban canals, shallow salt-marsh areas and open water as tidal channels. Total Hg was determined by cold vapour atomic fluorescence spectroscopy (CVAFS) and  $\text{CH}_3\text{Hg}$  using aqueous ethylation, GC separation and CVAFS detection.

Water was found to range from 0.8 to 135 ng/L in Hg, with 80-99% of that adsorbed to particles. Mercury was strongly correlated with total suspended solids (TSS) levels, which peaked in the summer, due perhaps to greater turbulence caused by increased boating and activities. Aqueous  $\text{CH}_3\text{Hg}$  showed a similar pattern, but with only 40-80% in the suspended phase. Because of the seasonality in TSS, Hg and  $\text{CH}_3\text{Hg}$  in the water column showed similar patterns, with 3-fold higher concentrations in summer compared to winter. A summer enrichment in  $\text{CH}_3\text{Hg}$ , which suggests greater methylation, is more clearly illustrated with the suspended Hg concentrations (6-fold increase) as compared to the aqueous samples. Total Hg in suspended matter did not show a discernible trend with season or location, randomly averaging about 1,760 ng/g, which is somewhat higher than the average surface sediment Hg concentration of 1,070 ng/g over the same region.  $\text{CH}_3\text{Hg}$ , on the other hand was much higher in the suspended matter (9.33 ng/g average) compared to the surface sediments (1.17 ng/g).