IAEA-SM-361/79P XA9950168

MAPPING SPATIAL VARIABILITY IN REDOX CONDITIONS AT THE LANDSCAPE SCALE USING THE STABLE ISOTOPIC COMPOSITIONS OF BIOTA

C. KENDALL, C.C. CHANG, S.R. SILVA
United States Geological Survey, Menlo Park, California, USA

Biochemical reactions such as denitrification and methyl mercury production in the shallow subsurface sediments in aquatic systems and watersheds can have profound effects on surface-water quality. These processes are controlled by redox conditions in the sediments or water column and, hence, may be strongly affected by transient changes in oxygen, nutrient, and trace element levels caused by seasonal changes in hydrology and anthropogenic inputs. Because of the ephemeral nature of chemical signals produced by these reactions, it is often difficult to assess the spatial and temporal extent of environmental conditions that favor these reactions, or the degree to which these reactions affect ambient water quality, by conventional chemical or isotopic measurements of dissolved species.

We are attempting to use the $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ of biota in marshes and riverine systems as indicators of local environmental conditions that may impact water quality. The theoretical basis of this study is that the isotopic compositions of plankton and non-fixing plants reflect to a large extent the isotopic compositions of the dissolved N, C, and S in the environment that is being utilized by the biota, as modified by various possible fractionating mechanisms in the plants. The isotopic compositions of the primary producers are then reflected by higher level organisms such as invertebrates and fish, as modified by mixed diets, trophic enrichments, and the larger foraging areas and time periods of the higher level organisms. Hence, under favorable conditions, the biomass isotopic compositions can reflect (and integrate) the extent of such processes as denitrification, sulfate reduction, and methane oxidation in the riparian zone, hyporheic zone, and water column that affect the isotopic compositions of the dissolved species.

Three major pilot studies are underway to test this hypothesis: in the Everglades (a large marsh in southern Florida), the Mississippi River Basin, and at the national scale. In each, broad regional surveys are coupled with site-specific studies to link biogeochemical processes with the biomass isotope patterns. At more than 100 marsh sites throughout the Everglades, representative algae, fish, and sediment samples were collected and analyzed for $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ to assess possible spatial, seasonal, and longer-term temporal changes in environmental conditions that favor methyl mercury production and bioaccumulation up the foodweb. In the Mississippi River Basin, where high nitrate levels in stream water pose potential problems for water supplies in the region and are suspected of causing a large hypoxic zone in the Gulf of Mexico each summer, we are investigating several isotopic approaches for tracing the nutrient sources and land uses that are contributing N to the Gulf of Mexico, and the N recycling processes that are reducing nitrate loads. Seasonal samples were collected at several dozen water-quality monitoring sites draining basins with different land uses and analyzed for the $\delta^{18}O$ and $\delta^{15}N$ of nitrate, and the $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ of particulate organic matter, dissolved organic matter, algae, fish, and invertebrates. This investigation of the usefulness of biomass isotopes as indicators of environmental conditions has been extended to the national scale by piggybacking on national sampling programs to collect and analyze samples of POM, fish, and invertebrates from over 100 additional sites.

In the Everglades, fish and algae both show wide ranges in isotopic composition throughout the marshes, with about a 10‰ range in δ values for each isotope and species. However, the spatial contour plots of the isotopic compositions display intriguing regional patterns that show little change with species or season. This is strong evidence that the environmental patterns reflected by the primary producers are being incorporated up the foodweb. The isotopic values show a general correspondence with peat thickness, with the lowest $\delta^{13}C$ values and highest $\delta^{34}S$ values along the major axis of the flow system. Areas with high methyl mercury contents commonly have high $\delta^{15}N$ and $\delta^{34}S$ values. Zones frequently dominated by particular redox reactions appear to be "labeled" by the $\delta^{13}C$, $\delta^{15}N$, and especially the $\delta^{34}S$ of local organisms. The spatial patterns in the modern biota are very different from the patterns in the upper 10 cm of the underlying peat, suggesting that the biota patterns reflect recent changes in environmental conditions.