

Carbon and Nitrogen Stable Isotope Tracing of Biogeochemical Processes in Eutrophic Lake Lugano, Switzerland

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Stable carbon and nitrogen isotopic studies have proven to be a powerful tool to better understand the biologically-driven carbon and nitrogen cycles in aquatic environments. In addition, through the stable isotopic analysis of sediments, insights can be gained on the trophic evolution of lakes, provided that the processes controlling isotope fractionation during organic matter formation and degradation are well understood. To date, the available data on the annual variability of nitrogen isotopic composition of lacustrine organic and inorganic species are very scarce, and the factors controlling the nitrogen isotopic composition of lacustrine organic matter are still poorly understood. In light of this deficit, we proposed to measure the isotopic composition of dissolved and particulate nitrogen and carbon species during a one-year period in Lake Lugano, a eutrophic lake in southern Switzerland. In particular, we aimed to characterize the most important controls on isotopic fractionation during the synthesis of organic matter in the photic zone and to evaluate possible isotopic alterations by different degradation processes in the water column.

Lake Lugano is monomictic, 91 m deep at the sampling station, and characterized by the progressive development of anoxic bottom waters between June and December due to the high primary productivity levels. Denitrification processes in the anoxic zone are evidenced by a progressive nitrate depletion associated with the development of anoxia in the bottom waters. Nitrogen and carbon isotopic compositions of sections vary strongly with time and depth, with $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values ranging between -5 and 20‰ and -60 and -24‰, respectively. During spring and summer, the $\delta^{15}\text{N}$ of the primarily autochthonous organic matter (OM) collected from the photic zone shows values between 2 and 7‰. These variations can be attributed to

isotope effects associated with nitrate uptake and N_2 fixation by cyanobacteria. The $\delta^{13}\text{C}$ value of OM increases from -34 to -24.5‰ as a response to the progressive development of productivity. An increasing trend in $\delta^{15}\text{N}$ with depth is observed, probably due to the progressive alteration of the OM, whereas carbon isotopes show no major variations with depth when the water column remains oxic.

With the development of anoxia, sections in the bottom waters shows very negative $\delta^{13}\text{C}$ values of up to -60‰, indicating that as much as 80% of the OM at these depths is synthesized in the water column by aerobic and/or anaerobic bacteria utilizing methane as their carbon source. Relatively depleted $^{15}\text{N}/^{14}\text{N}$ ratios ($\delta^{15}\text{N} = -5$ to 0‰) determined for this bacterial organic matter are probably due to the incorporation of ^{15}N depleted ammonium nitrogen derived from mineralization of sedimentary OM. Both the carbon and nitrogen stable isotopic ratios allow us to trace a "bacterioclinal", which is rising with the expanding volume of bottom-water anoxia during periods of stagnation.

Associated with the development of anaerobic conditions and coupled to decreasing $[\text{NO}_3^-]$, the $\delta^{15}\text{N}$ value of dissolved nitrate in the bottom waters is progressively increasing from 8‰ to 29‰ between June and August. This isotopic enrichment indicates active denitrification in the hypolimnion. Modeling of the evolution of the nitrate composition with a Rayleigh distillation model indicates a fractionation factor for the process of denitrification in the water column of approximately $14 \pm 1\%$. This study demonstrates the high potential of natural abundance-level measurements of carbon and nitrogen isotopic composition of OM and nitrate to trace biogeochemical processes in lakes.