



New insights into benthic nitrogen cycling using natural-abundance stable isotopes measurements

Alessandra Mazzoli¹, Cameron M. Callbeck¹, Tim J. Paulus¹, Claudia Frey¹, Jakob Zopfi¹, Sergei Katsev², Donald E. Canfield³, and Moritz F. Lehmann¹

¹Department of Environmental Sciences, University of Basel, Basel, Switzerland (alessandra.mazzoli@unibas.ch)

²Large Lakes Observatory, University of Minnesota, Duluth MN, USA

³Nordic Center for Earth Evolution, University of Southern Denmark, Odense M, Denmark

Marine and lacustrine benthic habitats represent hotspots of nitrogen (N) turnover, with many N transformation processes occurring simultaneously, and at high rates. More specifically, sedimentary microbial reduction of nitrate to dinitrogen (N₂), and other modes of N₂ production (e.g., anammox), are the most important sinks of fixed N in aquatic environments. Natural abundance stable isotope ratio measurements can be employed to help disentangling N-loss mechanisms, given that the isotope effects (ϵ) associated with each process are well studied.

In our study, we surveyed an array of lacustrine and marine benthic environments and assessed the isotopic composition ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) of porewater ammonium (NH₄⁺) and nitrate (NO₃⁻) – the key substrates driving the various N transformation pathways, such as denitrification, anammox, nitrification and dissimilatory nitrate reduction to ammonium (DNRA). We further examined how benthic N isotope dynamics vary in different sedimentary regimes, with distinct organic matter (OM) mineralization rates. We expect the relative importance of the various N pathways to affect the NH₄⁺ and/or NO₃⁻ isotope pools differentially.

Our preliminary porewater $\delta^{15}\text{N-NH}_4^+$ results suggest a diverse pattern with regard to the isotope enrichments between oligotrophic lakes, characterized by relatively strong depth gradients, and eutrophic lakes, where no significant depth gradient was observed. We hypothesize that this distinction could be attributed to different organic N availability and/or anammox contributions in the surveyed environments. Furthermore, we compared rate measurements (based on ¹⁵N addition experiments) to the N and O nitrate isotopic signatures to quantify processes, such as denitrification and DNRA. To investigate N isotope fractionation within the narrow nitracline, we employed the whole-core squeeze method, which provided a high-resolution porewater NO₃⁻ profile. Using this method, we found that the calculated community nitrate consumption ϵ values at the nitracline ($\epsilon_{\text{elim_porewater}}$) showed strong variability among the surveyed settings. We attribute such variation to shifts in the relative importance of denitrification versus DNRA and anammox between lakes of different trophic states. Overall, $\epsilon_{\text{elim_porewater}}$ was considerably below 25‰ – the value generally reported for the biological isotope effect of denitrification (ϵ_{denit}).