



Research Project

Expression of benthic isotope effects associated with nitrogen elimination and regeneration in lacustrine sediments

Third-party funded project

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Principal Investigator(s) [Lehmann, Moritz](#) ;

Project Members [Zopfi, Jakob](#) ; [Frey, Claudia](#) ; [Paulus, Tim](#) ; [Callbeck, Cameron](#) ; [Mazzoli, Alessandra](#) ;

Organisation / Research unit

Departement Umweltwissenschaften / Aquatic and Isotope Biogeochemistry (Lehmann)

Department

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In many ocean regions, as a limiting nutrient, bioavailable nitrogen (N) controls marine primary productivity and thus the ocean's capacity to fix and sequester atmospheric CO₂ in its interior. In many lakes, N from both natural and anthropogenic sources is an important driver of eutrophication. Therefore, both in the ocean and in lakes, it is crucial to understand the sources and sinks of fixed N. Denitrification, the microbial reduction of nitrate to dinitrogen (N₂), and other modes of suboxic N₂ production (e.g., the anaerobic oxidation of ammonium, or anammox), are the most important sinks of fixed N in aquatic environments, but particularly with regards to the N cycle in the ocean, there is a persistent debate regarding the overall size of sinks and sources.

Isotope ratios of nitrogenous species (e.g., ¹⁵N/¹⁴N) can provide important constraints on the natural N cycle. In order to use stable isotope measurements as a means to trace fluxes of N in aquatic systems, however, it is imperative to understand the isotope effects associated with these fluxes. While denitrification at the organism-level is known to be associated with a marked N isotope fractionation, the expression of the N isotope effect of benthic (i.e., sedimentary) denitrification in the water column above is only poorly constrained, and likely varies with the environmental conditions. Moreover, the possible impacts of other benthic N cycling processes on the N isotope exchange between the sediments and the water column (e.g., anammox, nitrate reduction to ammonium (DNRA), nitrate uptake, and/or nitrate regeneration) remain uncertain. Understanding the overall N isotope effect of net benthic N loss is a prerequisite for using N isotope measurements to infer its relative importance in the N cycle, in the global ocean or in a specific environment.

Here we propose an in-depth investigation of the isotope effects of benthic fixed N elimination and nitrate regeneration in aquatic sediments. The prime goal of the proposed research is to build a thorough understanding of the modulating controls on the nitrate and nitrite N (and O) isotope signatures of denitrification and anammox (and the interacting effects from other benthic N cycling reactions), and the N isotopic composition of gaseous N (i.e., N₂ and N₂O) that is ultimately lost from the sediments. We predict that the expression of the biological isotope effect of benthic N elimination at the level of sediment-water exchange will vary across different environments, and will strongly depend on the reactivity of the sediments, the O₂ penetration, the physical boundary conditions (i.e., diffusive transport), and on the extent to which other processes than denitrification contribute to the overall N cycling (nitrification, anammox, DNRA). Combining **1.) laboratory experiments with natural and artificial sediments, 2.)**

field investigations into the sediment porewater (N and O) isotope dynamics of distinct lacustrine and marine denitrifying benthic environments, and 3.) mathematical modeling, and making use of innovative multi-isotope techniques (natural abundance isotope analysis of $\text{NO}_3^- / \text{NO}_2^-$, ammonium, dissolved organic N, and N_2O , as well as ^{15}N tracer experiments), we attempt to gain complementary information on how the combined isotope effects of benthic nitrate reduction and nitrate regeneration are expressed in the water column of lakes and the ocean. With the diagenetic porewater N isotope model that this project will deliver we will establish a quantitative framework for assessing benthic isotope fluxes and for verifying our hypotheses.

The research proposed will result in the first comprehensive characterization of sediment pore-water N (and O) isotope dynamics in lacustrine settings, and will allow experimental constraints on the variability of N isotope effects during benthic nitrate reduction across different biogeochemical regimes. While the field component of the project focuses on lake sediments, the results expected will be directly pertinent to understanding of fixed-N elimination isotope effects in the ocean. It will thus be highly relevant for the use of N isotope measurements for local, regional, and even global N budgets, and will provide the basis for both paleolimnological and -oceanographic extrapolation.

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