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Fe2+, Mn2+ and H2S as electron donors for benthic N-processes in lacustrine sediments

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Intensive human activities have led to the increase of fixed N concentrations in many aquatic environments. Microorganisms help to mitigate N-loading in lakes by eliminating reactive nitrogen, mostly through anaerobic N_2 production within lacustrine sediments where bacterial densities are particularly high. The most important N sinks in lakes that transform fixed N (e.g. NO_3^-, NO_2^-, NH_4^+) to N_2 are denitrification and anammox. In contrast, dissimilatory nitrate reduction to ammonium (DNRA) retains bioavailable N within the system. The relative partitioning between nitrogen removal through denitrification and/or anammox, and its recycling via DNRA is an important modulator of internal eutrophication, and highly relevant for N balances in lakes. During canonical denitrification and DNRA, microorganisms use mainly organic matter for reducing nitrate, yet H_2S, Fe^{2+}, and/or Mn^{2+} are potential alternative electron donors. Recent work on DNRA in estuarine sediments has revealed the coupling of nitrate reduction and iron oxidation, but the importance of Fe^{2+}-dependent DNRA in lacustrine sediments remains uncertain. Similarly, sulfide-dependent nitrate reduction has been found to occur in freshwater sediments, though this process remains under-investigated. To our knowledge, there is no clear evidence for nitrate reduction in association with the oxidation of reduced manganese in lakes. The goal of this study was to quantify benthic NO_3^- reduction pathways in the lacustrine sediments of eutrophic Lake Lugano, and to investigate if, and to what extent, H_2S, Fe^{2+}, and/or Mn^{2+} control denitrification, anammox and DNRA. Laboratory incubation experiments were conducted with benthic microbial biomass from the sediments, $^{15}NO_3$- (100 μM) and addition of dissolved Fe^{2+}, Mn^{2+} or H_2S (500, 500 and 100 μM, respectively) at two different sites, Figino (Fe^{2+}/Mn^{2+}-rich) and Melide (Mn^{2+}-rich). These experiments revealed that at both locations, denitrification is the main nitrate-reducing pathway, with 5-8 times higher transformation rates than for DNRA. Anammox was negligible at both sites. In Figino, Fe^{2+} addition seemed to inhibit denitrification, while enhancing DNRA compared to the control experiment. The addition of Mn^{2+} did not have any effect on nitrate reduction, neither via denitrification nor DNRA. In Melide, but not in Figino, H_2S amendment considerably increased both denitrification and DNRA. This indicates that locally, chemolithotrophic denitrification and DNRA play a significant role for benthic N turnover, and suggests different microbial communities at the two sites. The exact biogeochemical controls on benthic microbial communities, the different impact of H_2S at the two sites, and, in particular the differential effect of Fe^{2+} on denitrification versus DNRA await further investigation through phylogenetic analyses and additional incubation experiments with ^{15}N labeled substrates.