

Interconnected biotic and abiotic nitrogen cycling pathways in a sulfate-rich lake: insights from geochemical and isotopic characterization

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The interconnection between biotic and abiotic pathways involving the nitrogen and iron biogeochemical cycles has recently gained interest. One of the reasons is that nitrite can be reduced abiotically (chemodenitrification) and biotically (denitrification) by ferrous iron oxidation. Lacustrine ecosystems are considered prone to denitrification, but its potential for promoting chemodenitrification is not well constrained. Since oxygen availability as well as the presence of iron, organic carbon and sulfur compounds are suspected to play an important role, an integrative study was performed in Gallocanta Lake (Spain) in order to improve our knowledge on these complex pathways.

Gallocanta Lake is an ephemeral and endorheic saline lake with significant organic matter inputs. Bacterial sulfate reduction occurs near the water-sediment interface but sulfate concentrations increase with sediment depth due to mineral dissolution. Moreover, up to 0.1 mM dissolved iron was measured in porewater ($\text{Fe}^{2+} + \text{Fe}^{3+}$). The peak was found at 7 cm depth, pointing to a possible involvement with denitrification and chemodenitrification. In this context, several sets of anoxic batch experiments were performed using surface water and sediment from the lake. The potential for denitrification and/or dissimilatory nitrate reduction to ammonium (DNRA) was tested by nitrate injection at 100 and 500 μM , for chemodenitrification nitrite was injected at 500 μM with or without addition of ferrous iron, for ammonification no injection was made.

Geochemical data confirmed the potential for ammonification (4 μM ammonium release, 33 hours), pointed to the co-occurrence of DNRA and denitrification (nearly complete nitrate reduction, nitrite and ammonium accumulation, 50 hours), and suggested a chemodenitrification contribution to nitrite attenuation (40 % nitrite reduction, 67 hours). Initial calculations on isotopic fractionation showed values ranging among those reported for denitrification for nitrate ($\epsilon^{15}\text{N} = -12$ to -9 ‰, $\epsilon^{18}\text{O} =$

-15 to -10 ‰), and close to those reported for both the biotic and abiotic reduction for nitrite ($\epsilon^{15}\text{N} = -12$ to $+2$ ‰). Isotopic mass balance and fractionation extent allows to propose an accurate N cycling scheme for Gallocanta lake which exhibits a close relationship with the carbon, sulfur and iron cycles in such atypical aquatic system.