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Iron-mediated nitrite reduction as a major sink of reactive nitrogen across contrasting lakes

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The coupling between nitrogen and iron cycling regulates reactive nitrogen turnover in aquatic environments; however, its relevance in natural systems is still not fully understood. Ferrous iron drives nitrite reduction through chemodenitrification and iron-mediated denitrification, directly regulating nitrogen speciation, redox evolution, and nitrogen retention in sediments. Lacustrine systems, structured by steep physicochemical gradients and dynamic sediment–water exchange, provide powerful natural laboratories to resolve iron-driven nitrogen transformations.

To determine the extent of iron-driven chemodenitrification across redox regimes, we build on a fully characterized saline reference system [1] and extend the investigation to two contrasting freshwater lakes. Specifically, the endorheic saline Lake Gallocanta (Spain), enriched in sulfate and organic matter; the anthropogenically influenced freshwater Lake Biscarrosse (France); and the oligotrophic alpine Lake Gentau (France), characterized by elevated dissolved iron availability.

Depth-resolved water column and sediment porewater geochemical profiles revealed site-specific redox regimes largely structured by iron availability. Gallocanta is characterized by sulfate-rich porewaters, whereas Gentau displays pronounced iron reduction with elevated ferrous iron and ammonium concentrations. Biscarrosse shows intermediate sulfate and iron levels but comparatively lower organic carbon and ammonium enrichment.

Anoxic microcosm incubations demonstrate active nitrate and nitrite reduction in all lakes and identify chemodenitrification as a consistent contributor to nitrite consumption alongside denitrification and DNRA. Reduction rates follow the order Gallocanta ≈ Biscarrosse > Gentau, reflecting the combined influence of iron availability, organic carbon content, and redox zonation. Iron-driven nitrite transformation systematically links Fe(II) oxidation to nitrogen partitioning and reactive nitrogen removal.

Isotopic fractionation patterns derived from controlled experiments provide decisive constraints to distinguish abiotic chemodenitrification from microbial nitrite reduction. The integration of depth-resolved geochemistry, experimental kinetics, and isotopic tracing establishes mechanistic nitrogen–iron coupling schemes tailored to contrasting lacustrine settings.

This work demonstrates that iron-mediated nitrite reduction represents a relevant reactive nitrogen sink in lakes and defines the geochemical conditions that regulate its expression. The resulting framework strengthens predictive understanding of nitrogen turnover under variable redox and iron regimes and provides robust constraints for coupled iron and nitrogen cycling in aquatic systems.

[1] Margalef-Marti, et al. Chemosphere 359 (2024), 142292