



## **A case study of nitrification and nitrite isotope fractionation in a eutrophic temperate river system**

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Stable isotopes of nitrate are often used to assess processing of nitrate in the water column of oceans, estuaries, and rivers. In all these environments, nitrate regeneration via nitrification is an important source of new nitrate. The bulk isotope effect of nitrification is hard to predict: It is a two-step-process by distinct groups of microorganisms oxidizing ammonium to nitrate via nitrite. Both processes have divergent isotope effects, and it is even more difficult to unravel these effects in natural environments, because nitrite usually does not accumulate and isotope analysis is not possible.

During our routine sampling scheme at the River Elbe an exceptional flood occurred in June 2013, and nitrite and ammonium accumulated, allowing us to investigate isotope fractionation of nitrification in a natural river system. We measured nutrient concentrations, dual nitrate isotopes,  $\delta^{15}\text{N-NO}_2$ , and, where possible,  $\delta^{15}\text{N-NH}_4$ .

Nitrate leached from catchment area, and  $\delta^{15}\text{N-NO}_3$  and  $\delta^{18}\text{O-NO}_3$  decreased from typical spring bloom values (9.0 ‰ and 3.5 ‰ respectively) to winter nitrate background values (7.4 ‰ and 2.1 ‰ respectively). This indicates that riverine assimilation was minimal during the flood. Ammonium and nitrite concentrations increased to 12.5  $\mu\text{M}$  and 5.7  $\mu\text{M}$ , respectively, which likely was due to remineralization and nitrification in the water column. Ammonium  $\delta^{15}\text{N-NH}_4$  values increased up to 12 ‰ and nitrite  $\delta^{15}\text{N-NO}_2$  values ranged from -4.8 ‰ and -14.2 ‰. Nitrite oxidation and decreasing concentrations were coupled with a fractionation factor  $15\epsilon$  of -8.6 ‰ following normal, and not inverse, isotope fractionation. This deviates from findings in pure cultures of nitrite-oxidizing bacteria. We assume that the mechanisms responsible for inverse fractionation apply in natural environment as well, but that the resulting trend in  $\delta^{15}\text{N-NO}_2$  is masked by dilution with fresh nitrite stemming from ammonium oxidation. Our data are a first approximation of the natural bulk isotope effect of nitrite oxidation in natural environments and highlight that pure culture results cannot easily be extrapolated to natural microbial assemblages or water bodies.