

Oxygen Isotopic Composition of Nitrate Produced by Freshwater Nitrification

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Measurements of naturally occurring nitrogen and oxygen stable isotope ratios of nitrate (NO_3^-), $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, can be used to determine the source, dispersal, and fate of natural and contaminant NO_3^- in aquatic environments. To this end, it is necessary to know how NO_3^- isotopologues are modified by biological reactions, as heavy and light isotopes have different reaction rates. The purpose of this study was to determine the influence of the $\delta^{18}\text{O}$ of ambient water on the isotopic composition of NO_3^- produced by nitrification, the biological oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) then NO_3^- , an influence which is not well understood in freshwater systems. We collected water from two streams in New England during the fall and spring, which we amended with NH_4^+ and with increments of ^{18}O -enriched water, and then monitored the isotopic composition of NO_2^- and NO_3^- produced by natural consortia of nitrifiers. Although oxidation rates differed between the two stream waters, the final $\delta^{18}\text{O}$ of NO_3^- produced in both experiments revealed a sensitivity to the $\delta^{18}\text{O}$ of water mediated by (a) isotopic equilibration between water and NO_2^- and (b) kinetic isotope fractionation during O-atom incorporation from molecular oxygen and water into NO_2^- and NO_3^- . Our results concur with nitrifying culture experiments that have demonstrated analogous sensitivity of the $\delta^{18}\text{O}$ of NO_3^- product to equilibrium and kinetic O isotope effects (Buchwald et al. 2012). These dynamics need to be understood to interpret NO_3^- isotope distribution in freshwater environments.