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Isotopic signals of denitrification in a northern hardwood forested catchment

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Water samples from streams, groundwater and precipitation were collected during summer from the hydrologic reference watershed (W3) at Hubbard Brook Experimental Forest in the White Mountains, New Hampshire, and analysed for d15N-NO_3 and d18O-NO_3. Despite very low nitrate concentrations (<0.5 to 8.8 uM NO_3-) dual-isotopic signals of sources and processes were clearly distinguishable. The isotopic composition of nitrate from shallow groundwater showed evidence of dual isotopic fractionation in line with denitrification, with a positive relationship between nitrogen and oxygen isotopic composition, a regression line slope of 0.76 (r2 = 0.68), and an empirical isotope enrichment factor of εP-S 15N-NO_3 -12.7%. The isotopic composition of riparian groundwater nitrate from time-series samples showed variation in processes over a small spatial scale.

The expected isotopic composition of nitrate sources in the watershed was used to distinguish nitrate in rain and nitrate from nitrification of both rainfall ammonium and ammonium from mineralised soil organic nitrogen. Evidence of oxygen exchange with water during nitrification was seen in the isotopic composition of stream and shallow groundwater nitrate. The isotopic composition of streamwater nitrate following a period of storms indicated that 25% of nitrate in the streamwater was of atmospheric origin. This suggests rapid infiltration of rainfall via vertical bypass flow to the saturated zone, enabling transport of atmospheric nitrate to the stream channels.

Across the Hubbard Brook basin, the isotopic composition of nitrate from paired samples from watersheds 4-7 indicated a switch between a nitrification and assimilation dominated system, to a system influenced by rainfall nitrogen inputs and denitrification.
The dual isotope approach has revealed evidence of denitrification of nitrate from different sources at low concentrations at Hubbard Brook during summer. This isotopic evidence deepens our understanding of the significance and spatial variability of denitrification in environments with low levels of nitrate, represented by this northern hardwood forested catchment.