Isotopic overprinting of nitrification on denitrification as a ubiquitous and unifying feature of nitrogen cycling across landscapes

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Nitrogen and oxygen isotopes of NO_3^- ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) have provided an invaluable tool for evaluating its sources and transformations in the environment for over three decades. Nevertheless, conventional interpretations of NO_3^- isotope distributions appear at odds with patterns emerging from studies of nitrifying and denitrifying cultures. We present a numerical model of NO_3^- isotope dynamics, demonstrating that deviations in $\delta^{18}O_{NO3}$ *vs*. $\delta^{15}N_{NO3}$ from a 'trajectory' of 1 expected for denitrification must stem from isotopic over-printing by coincident NO_3^- production by nitrification and/or anammox. Our analysis highlights two central parameters: 1) the $\delta^{18}O$ of ambient water and its degree of incorporation during NO_2^- oxidation and 2) the relative flux of NO_3^- production under net denitrifying conditions. Dual isotopic trajectories >1, characteristic of marine denitrifying systems, arise mainly under elevated NO_2^- re-oxidation relative to NO_3^- reduction (>50%) and in association with the high $\delta^{18}O$ of seawater. This implicates nitrification as the major NO_3^- producing term in marine denitrifying systems. In contrast, trajectories <1 comprise the greater majority of model solutions, with representative aquifer conditions requiring lower NO_2^- re-oxidation fluxes (<15%) and the influence of the lower $\delta^{18}O$ of freshwater. We suggest that widely observed $\delta^{18}O_{NO3}$ *vs*. $\delta^{15}N_{NO3}$ trends in freshwater systems (always <1) must result from concurrent NO_3^- production by anammox in anoxic aquifers, a process that has been largely overlooked.