# Nitrogen and oxygen isotopomeric constraints on the sources of nitrous oxide and the role of submarine groundwater discharge in a temperate eutrophic salt-wedge estuary



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Estuaries have been identified as sources of nitrous oxide (N2O) emissions to the atmosphere but questions remain as to which production pathway(s) govern the oversaturation of N2O observed in most estuaries worldwide. Here, we use a suite of nitrate and N2O isotopes, as well as the N-15 site preference signatures of N2O to assess (1) the relative importance of different N2O production pathways in a eutrophic groundwater-impacted salt-wedge estuary and the aquifers underlying the estuary and (2) the influence of groundwater input on the overall N2O saturation in the estuary. This is one of the few studies to examine the effect of groundwater-surface water interaction on N2O cycling using N2O isotopes. The site preference values of N2O in the deep aquifer below the estuary were distinctive (83 parts per thousand +/- 25 parts per thousand) and were much higher than in either surface water (21 parts per thousand +/- 6 parts per thousand) or shallow groundwater (44 parts per thousand +/- 8 parts per thousand), suggesting the influence of multiple biotic and/or abiotic processes which proceed through multiple cycles, and/or the occurrence of a yet unidentified N2O production pathway. Isotope endmember considerations revealed that nitrifier-denitrification was the major N2O production pathway within the shallow aquifer whereas within the estuarine water column, N2O saturation was governed by chemodenitrification and discharge of N2O-laden submarine groundwater. Our study not only emphasizes the substantial, yet often underappreciated role of submarine groundwater discharge in estuarine N2O budgets, but also highlights the need to reevaluate the importance of the noncanonical denitrification pathways (i.e., chemodenitrification and nitrifier-denitrification) in controlling the overall N2O production from estuarine and groundwater environments.
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