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# Nitrate isotopic composition and ancillary variables (land use, redox, excess N2, age, water isotopics) in California groundwater

Nathan Veale (1), Jean Moran (1), Ate Visser (2), Michael Singleton (2), and Bradley Esser (2)

(1) California State University, East Bay, Hayward, CA, United States , (2) Lawrence Livermore National Laboratory, Livermore, CA, United State

Nitrate is a critical water quality issue in California, the United States and the world. Lawrence Livermore National Laboratory (LLNL) has compiled a large, unique database of California groundwater nitrate isotopic compositions ($\delta$15N-$NO_3$ and $\delta$18O-$NO_3$), acquired largely through more than a decade of coordination with the State of California Groundwater Ambient Monitoring and Assessment (GAMA) program. The water samples are predominantly from shallow aquifers accessed by domestic and monitoring wells. The database of >1,300 nitrate isotopic compositions includes a number of important ancillary parameters: DO, ORP and DOC (measured for 18% of samples); excess air and dissolved N2 (24%); water isotopic composition ($\delta$18O-$H_2O$ and $\delta$D-$H_2O$) (43%); and tritium/3He groundwater age (27%). Methods used at LLNL include sample preparation by the denitrifier method (for $\delta$15N-$NO_3$ and $\delta$18O-$NO_3$) and Isotope Ratio Mass Spectrometry with ($\delta$15N-$NO_3$ and $\delta$18O-$NO_3$ and $\delta$18O-$H_2O$ and $\delta$D-$H_2O$), Noble Gas Mass Spectrometry (NGMS; for excess air and groundwater age), and Membrane Inlet Mass Spectrometry (MIMS; for major dissolved gases and excess N2). Redox indicators (DO, ORP and DOC) in conjunction with excess N2, groundwater age, and nitrate isotopic composition are used to assess the presence or absence, and potentially the rate of, saturated-zone denitrification. Comparison of $\delta$18O-$NO_3$ to $\delta$18O-$H_2O$ isotopic composition is used to distinguish synthetic nitrate from nitrification of reduced forms of nitrogen as a source of groundwater nitrate. Groundwater age is used to discern timing and temporal trends in groundwater nitrate isotopic composition. The relationship of nitrate isotopic composition to ancillary parameters (redox, excess N2, water isotopic composition and groundwater age) is explored, along with its relationship to well location, screened interval, and land use, with a focus on the extent of saturated-zone denitrification and the significance of synthetic nitrate as a source of nitrate to California groundwater.