Nitrate in California Groundwater

Isotopic Composition and Spatial Denitrification Trends

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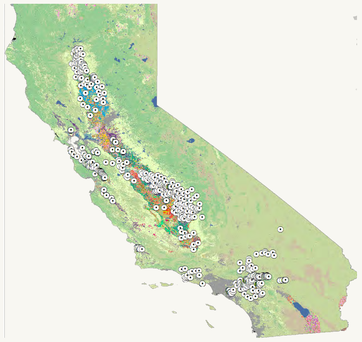
- Nitrate is a significant water quality issue in California.
- Critical to addressing nitrate contamination are both understanding the presence and extent of denitrification and further refining isotopic techniques used to identify nitrate sources
- LLNL, in coordination with the State of California GAMA program, has collected groundwater samples over a ten + year period
- This study aims to explore the utility of the oxygen isotope of nitrate ($\delta^{18}O\text{-}NO_3$-) as a source identification tool. Additionally, we attempt to explain the disconnect between isotopic groundwater values and a N mass balance approach to California's nitrate issues.

METHODS

LLNL samples were supplemented by USGS NWIS data to create a dataset of over 1,200 data points. Methods used at LLNL include sample preparation by the denitrifier method ($\delta^{15}N\text{-}NO_3$- and $\delta^{18}O\text{-}NO_3$-) and Isotope Ratio Mass Spectrometry ($\delta^{15}N\text{-}NO_3$- and $\delta^{18}O\text{-}NO_3$-and $\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$), Noble Gas Mass Spectrometry (excess air and N_2), and Membrane Inlet Mass Spectrometry (major dissolved gases and excess N_2) (**RIGHT**).

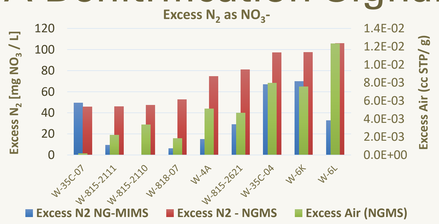


Spatial analytics was done using the ArcGIS platform, supplemented by statistical analysis in R and Excel. The USDA Cropland Data Layer provided land use attributes for each sample (**LEFT**).

Samples taken from LLNL Site 300 helped shed light on the accuracy differences between the NGMS and MIMS methods of quantifying excess N_2.

EXCESS N_2

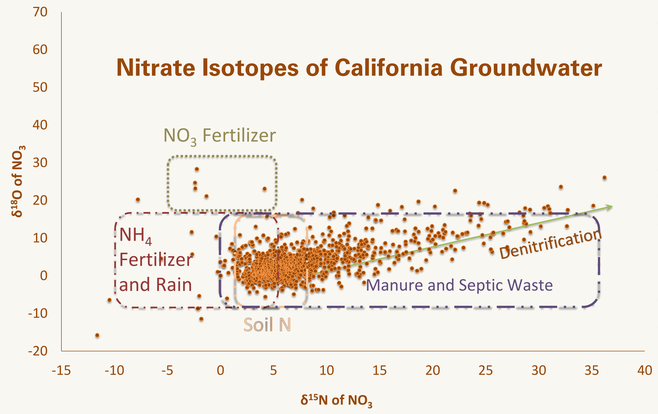
A Denitrification Signal



Excess N_2 as NO_3- in 9 wells measured by the NGMS and NG-MIMS. Excess air in green is measured using Ne and Xe values from NGMS. There is little correlation between the amount of excess air in a sample and the difference between instrument measurements.

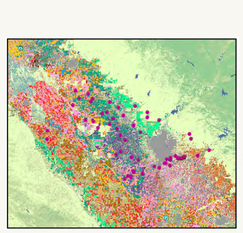
Though cost prohibitive and time intensive compared to the NG-MIMS, the NGMS provides an accurate, robust method of quantifying excess N_2. NGMS values were preferred in this study whenever possible.

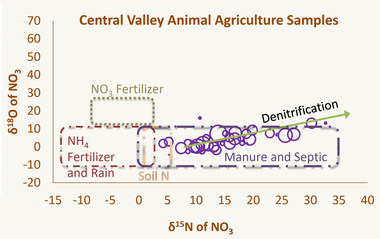
EVIDENCE OF PERVASIVE DENITRIFICATION

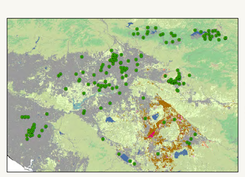


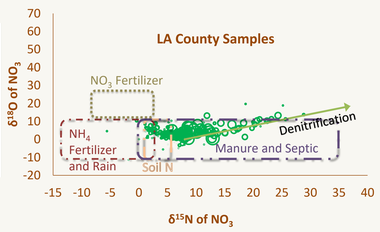
The statewide sample population trends along the 2:1 slope commonly associated with denitrification.

A substantial portion of the samples fall within the source zone for organic nitrate, despite the large amount of inorganic fertilizer applied to California croplands since the mid-20th century.





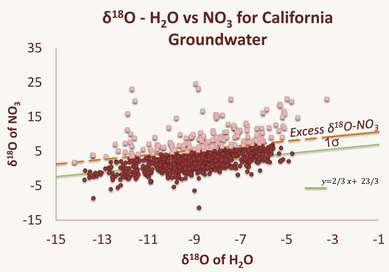




Dual nitrate isotope plots for two sample groupings, with sample points scaled for nitrate concentration. Both groups show a clear denitrification trend among the samples.

Two sources can be inferred from the Los Angeles plot; smaller nitrate concentrations, likely representing background levels from natural processes are clustered around 2-4 $\delta^{15}N\text{-}NO_3$, with a second cluster of larger nitrate concentrations forming between 5-12 $\delta^{15}N\text{-}NO_3$, likely from septic/wastewater sources.

ISOTOPIC SIGNATURES OF NITRATE-OXYGEN

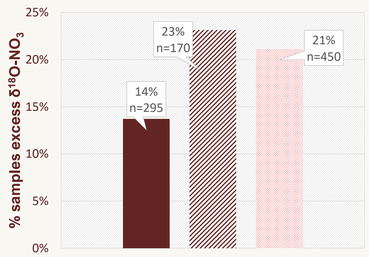


(1) $\delta^{18}O\text{-}NO_3^- = 1/3\ \delta^{18}O\text{-}O_2 + 2/3\ \delta^{18}O\text{-}H_2O$

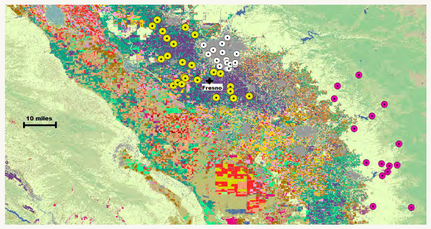
Eq. 1 describes the hypothetical relationship of nitrate-oxygen's isotopic ratio to the values for soil water and air-oxygen during nitrification

The solid green line represents equation 1, and the dashed orange line dubbed 'Excess' $\delta^{18}O\text{-}NO_3$- is one standard deviation away from the predicted value, and separates 'excess' samples.

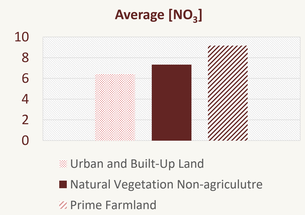
E



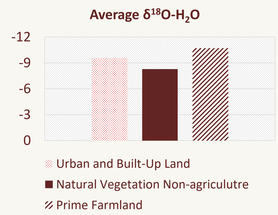
A



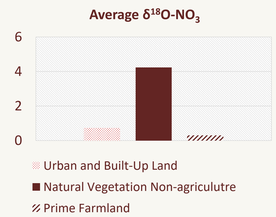
B



C



D



78% of our samples fell within 1σ of eq. 1's predicted value, indicating that, in general, samples follow the 2:1 paradigm. 3 sample subsets from California's central valley (**A**) were chosen to elucidate reasons for non-conforming, excess $\delta^{18}O$ values. Although nitrate concentrations (**B**) and water isotopes **(C)** fell in expected ranges, $\delta^{18}O\text{-}NO_3$ (**D**) did not. Contrary to our expectations and results from the complete dataset (**E**), samples in 'natural' settings had the highest deviations from eq. 1 in the central valley subset.

CONCLUSION Nitrogen Cycling and Transport

- 'Excess' $\delta^{18}O\text{-}NO_3$- samples, which accounted for ~22% of the sample population, occur across the spectrum of land use, at negligible and high concentrations of nitrate, areas with and without evidence for significant denitrification, and in locations lacking a proximate source of synthetic nitrate. We suggest the primary mechanism in these domains causing excess $\delta^{18}O$ is the mixing and transport of highly mobile nitrate molecules to water sources other than those they were nitrified in.
- The disconnect between N mass balance and the results of dual isotope nitrate plots is most probably twofold: some significant amount of denitrification, compounded with removal of the source signature through sequential cycles of nitrification/denitrification. Since other studies have concluded the effect of denitrification at regional scales in California is somewhat minimal (Landon et. al., 2011), further work is needed to address its significance