Introduction & Setting

Multiple sources of nitrate in Mortandad Canyon (up to 18.2 ppm) have been found in water samples collected from intermediate aquifers. Sources of nitrate potentially reaching the alluvial and intermediate aquifers include: (1) sewage effluent, (2) neutralized natural abundance nitric acid from a chemical waste treatment facility, (3) \( ^{15} \)N-depleted nitric acid, and (4) natural background nitrate. Each of these sources is unique in its \( \delta ^{15} \text{N} \) and \( \delta ^{18} \text{O} \) values. Using stable isotope ratios, a mixing model for the three anthropogenic sources of nitrate was established, allowing for an analysis of the relative contributions of each source to the nitrate concentrations observed in the intermediate aquifers.

Stable Isotope Ratios of NO\(_3\) sources

![Stable Isotope Ratios of NO\(_3\) sources](image)

The isotopic composition of nitrate from different sources can be used to identify the contributions of each source to the nitrate concentrations observed in the intermediate aquifers. The mixing model suggests a mixture of sewage effluent (0.8‰), neutralized nitric acid (1.2‰), and \( ^{15} \)N-depleted nitric acid (0.6‰) in the intermediate aquifers.

Results and Source Identification

Groundwater nitrate in both Mortandad Canyon aquifers show a very large range in \( \delta ^{15} \text{N} \) and \( \delta ^{18} \text{O} \), not observed in most natural settings. Typical distributions of nitrate N and O isotopes fall in a much smaller range (-5‰ to 25‰, 0‰ to 25‰). Nitrate is a conservative anion. Stable isotope ratio can be explained by mixing among 5 sources (assuming no denitrification).

Sampling

- 122 samples from Mortandad Canyon
  - 4 years of samples from 17 wells (2005-2009)
  - 7 alluvial wells (MT-1, MT-3,M-4, MCO-7, MCO-6, MCO-5, MCO-7, MCO-2)
- 4 intermediate wells (MCO-2, MCO-6, MCO-7, MCO-7, MCO-2)
- 186 wells & springs from the Pajarito Plateau as background.
- Treated effluent from RLWTF in August 2009.

Method for \( \delta ^{15} \text{N}\)-\( \delta ^{18} \text{O} \) in groundwater nitrate

- Automated microbial denitrification technique using Pseudomonas aeruginosa (ATCC 13031) (modified from Sigman et al. 2001)
- Future paper: preliminary development, inclusion of degradation of nitrite
- \( \delta ^{18} \text{O} \) converted to \( \delta ^{15} \text{N} \) in anoxic conditions
- Isotopic measurements of N\(_2\), NO\(_x\), N\(_2\)O, & NO by mass spectrometry
- N\(_2\)O mixtures for internal standardization
- Calibration of USGS, IAEA standards (USGS 32, 34, IAEA-NO\(_3\)-5, IAEA-NO\(_3\)-4)
- Minimum required concentration > 0.12 ppm NO\(_3\)-N.
- Presence of NO\(_3\) can affect \( \delta ^{15} \text{N} \) results.

Dentnitrification is unlikely in this setting.

- Most denitrogenated oxygen greater than 3.5 mg/L, which correlates greater than 45% denitrogenated oxygen saturation at the measured temperatures and pressures.
- Sulfate is present in measurable concentrations (10 to 39 mg/L).
- No detectable nitrite in any groundwater samples.
- Eh conditions controlled by the MnO\(_2\)/Fe\(_2\)O\(_3\) redox couples (0.8 and 1.2 V.) and calcium carbonate concentration 1.3 to 8 mg/L.
- Dissolved and total organic carbon is less than 2 mg/L.

Future work:

- Better understand isotopic variability in other anthropogenic sources at LANL and historic variability.
- Improve detection limits/precision, and analyze nitrite in background waters in anoxic environments.

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References

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Abstract

Multiple sources of nitrate in Mortandad Canyon (up to 18.2 ppm) have been found in water samples collected from intermediate aquifers. Sources of nitrate potentially reaching the alluvial and intermediate aquifers include: (1) sewage effluent, (2) neutralized natural abundance nitric acid from a chemical waste treatment facility, (3) \( ^{15} \)N-depleted neutralized nitric acid, and (4) natural background nitrate. Each of these sources is unique in its \( \delta ^{15} \text{N} \) and \( \delta ^{18} \text{O} \) values. Using stable isotope ratios, a mixing model for the three anthropogenic sources of nitrate was established, allowing for an analysis of the relative contributions of each source to the nitrate concentrations observed in the intermediate aquifers. The spatial and temporal variability in nitrate contamination sources through Mortandad Canyon is clearly shown in the resulting ternary plot. Whereas microbial denitrification has been shown to change nitrate stable isotope ratios in other settings, the Vadose potential, relatively high dissolved oxygen content, increasing nitrate concentrations over time, and lack of observed NO\(_2\) in these wells suggest minimal changes to the stable isotope ratios has occurred. Changes in the nitrate stable isotope ratios over time reflect changes in the volume of effluent released, and/or changes to the \( \delta ^{15} \text{N} \) and \( \delta ^{18} \text{O} \) values of nitric acid used during liquid waste processing. Temporal trends indicate that the earliest form of anthropogenic nitrate in this watershed was neutralized natural abundance nitric acid. Alluvial wells preserve a trend of decreasing nitrate concentrations and mixing models show decreasing contributions of \( ^{15} \)N-depleted nitric acid, consistent with smaller volumes of effluent released from the chemical waste treatment facility.

Nearby intermediate wells show increasing nitrate concentrations and mixing models indicate a larger component derived from \( ^{15} \)N-depleted nitric acid. These data indicate that the pulse of neutralized \( ^{15} \)N-depleted nitric acid that was released into Mortandad Canyon between 1986 and 1989 has infiltrated through the alluvium and is currently affecting two intermediate wells. This hypothesis is consistent with previous research suggesting that the perched intermediate aquifers in the Mortandad Canyon watershed are recharged locally from the alluvial aquifers.

Method for \( \delta ^{15} \text{N} \)-\( \delta ^{18} \text{O} \) in groundwater nitrate

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Future work:

- Better understand isotopic variability in other anthropogenic sources at LANL and historic variability.
- Improve detection limits/precision, and analyze nitrite in background waters in anoxic environments.

Using measured values and associated physical limits, a theoretical distribution of 500 random possible combinations of background-nitrate concentration, \( \delta ^{15} \text{N} \) and \( \delta ^{18} \text{O} \), values, were calculated using latin hypercube sampling (LHS). LHS is a stratified random sampling procedure that assures the full range of each distribution is sampled with a minimum number of samples. The set of 500 random background nitrate values used is the previously described background subtraction calculation to generate, in a probabilistic fashion, background-corrected stable isotope ratios for each sample.

Conclusions

- Chemical processing impacts distinct N and O isotope signatures that are preserved for years in aerobic groundwater systems.
- Downgradient alluvial wells show decreasing nitrate concentrations, and more \( ^{15} \)N depleted component from \( ^{15} \)N-depleted nitric acid. This suggests more of the mass of the plume has passed, and is consistent with smaller nitrate releases from the RLWTF.
- In intermediate aquifers, the \( ^{15} \)N-depleted nitric acid component has reached 2 of 3 wells, but is not seen in nearby MCO-6. Unexpected sewage effluent source in MCO-5. These indicate different recharge pathways for the intermediate aquifers.
- Mixing ratios in the intermediate wells trend toward those of the alluvial wells, indicating recharge from the alluvial to the intermediate aquifers.
- A probabilistic approach can be used to assess uncertainty and error. Future work will expand this to the anthropogenic sources.
- Fate and transport of multiple sources of a single nitrate contaminant can be quantified with robust knowledge of the isotopic compositions of the end members.
- A change in the isotopic composition of the effluent released from the RLWTF due to changing waste treatment processes and/or different chemists used during processing could confound apparent trends. This result is difficult to interpret in a mixed-source environment, without knowledge of other geochemical parameters.
- Downgradient groundwater has the potential to preserve stable isotope signatures of chemical processing.