Differentiation among Multiple Sources of Anthropogenic Nitrate in Mortandad Canyon, Pajarito Plateau, using Dual Stable Isotope Systematics

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Abstract

The groundwater system beneath Mortandad Canyon on the Pajarito Plateau has been affected by multiple sources of anthropogenic nitrate contamination. Average NO_3-N concentrations of up to 18.2±1.7 mg/L have been found in wells in one of the perched 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 $\delta^{18}O$ and $\delta^{15}N$ values. Using nitrate stable isotope ratios, a mixing model for the three anthropogenic sources of nitrate was established, after applying a linear subtraction of the background component.

The spatial and temporal variability in nitrate contaminant sources through Mortandad Canyon is clearly shown in the resulting ternary plots. Whereas microbial denitrification has been shown to change nitrate stable isotope ratios in other settings, the redox 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 $\delta^{15}N$ and $\delta^{18}O$ 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 15N-depleted nitric acid. These data indicate that the pulse of neutralized 15N-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.

Sampling

- 122 samples from Mortandad Canyon
- 4 years of samples from 17 wells (2005-2009)
- 7 alluvial wells: (MT-1, MT-3,MT-4, MCO-7.5, MCO-6, MCO-5, MCO-7, MCA-2)
- 4 intermediate wells (MCOI-4,-5,-6, SCI-1)
- 16 wells & springs from the Pajarito Plateau as background
- Treated effluent from RLWTF in August 2009.

Method *for $\delta^{15}N$-$\delta^{18}O$ in groundwater nitrate*

- Automated microbial denitrification technique using *Pseudomonas aureofaciens (ATCC# 13985)* (modified from Sigman et al. 2001)
- Culture preparation, colony development, inoculation
- NO_3 converted to $N_2O_{(g)}$ in anaerobic conditions
- Isotopic measurement of N_2O (*m/z* = 44,45,46)
  - TraceGas preconcentrator coupled to continuous flow-IRMS
  - High throughput (~15-20 samples/day)
- Data correction (blank correction, analytical drift)
- Calibration off USGS, IAEA standards (USGS 32,34, IAEA-NO3)
- Sample storage issues
  - Removal of DIC
  - Natural microbial denitrification after sampling
- Precision of ±0.25‰ for $\delta^{15}N$ and ±0.75‰ for $\delta^{18}O$

- Limitations:
  - Minimum required concentration >0.12 ppm NO_3-N.
  - Presence of NO_2^- can affect $\delta^{18}O$ results.

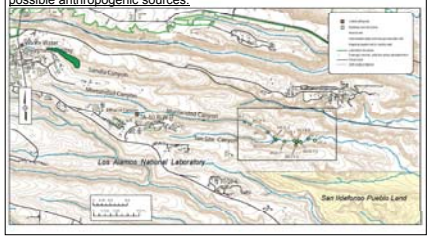
Introduction & Setting

Multiple sources of nitrate in Mortandad Canyon (up to 18.2 ppm)
Regional water table ~300m
The vadose zone contains 2 distinct water-saturated hydrologic zones;
Shallow alluvium at < 35m,
Several perched intermediate-depth zones at 125-200m.

The conceptual model invokes surface-water recharge into permeable alluvial sediments at the canyon bottoms, with infiltration along fractures to the perched intermediate aquifers.

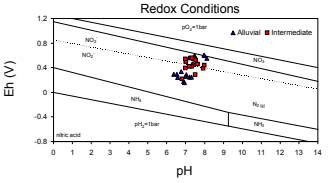
Possible sources of nitrate:
- Sewage effluent
- Chemical effluent from RLWTF, neutralized nitric acid (with isotopically light signature during some '86-'89 releases)
- Natural background nitrate

Each source is unique in $\delta^{15}N$, $\delta^{18}O$.
Stable isotopes of N & O can be used to distinguish contributions of possible anthropogenic sources.

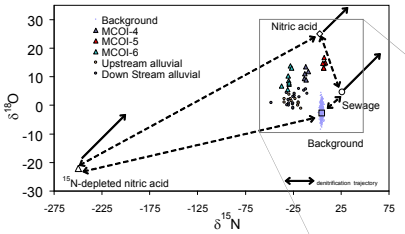


Denitrification is unlikely in this setting.

- Most dissolved oxygen concentrations greater than 3.5 mg/L, which correlates to greater than 45% dissolved oxygen saturation at the measured temperatures and pressures
- Sulfate is present in measurable concentrations (10 to 39 mg/L)
- No detected nitrite in any groundwater samples
- Eh conditions controlled by the MnO_2/Mn^{2+} and $Fe(OH)_3/Fe^{2+}$ redox couples (Fe^{2+} and Mn^{2+} concentrations average 131±260 µg/L and 13±30 µg/L, respectively)
- Dissolved and total organic carbon is less than 2 mg/L



Results and Source Identification



Groundwater nitrate in both Mortandad Canyon aquifers shows a very large range in $\delta^{18}O$ and $\delta^{15}N$, not observed in most natural settings.

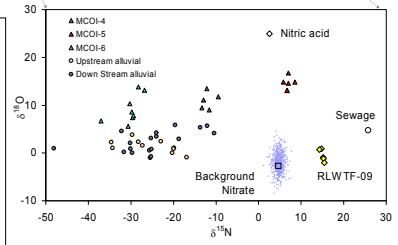
Typical distributions of nitrate N and O isotopes fall in a much smaller range ($\delta^{15}N$: -5‰ to 20‰; $\delta^{18}O$: 0‰ to 25‰).

Nitrate is a conservative anion. Nitrate stable isotope ratio can be explained by mixing among 4 sources (assuming no denitrification).

Stable Isotope Ratios of NO_3 sources

1. Nitric acid chemical discharge: based on average of 4 nitric acids used at LANL
2. ^{15}N-depleted nitric acid: lightest sample collected upgradient of study area
3. Sewage effluent: results from SCI-1, an intermediate-depth well downgradient from known sewage source in near canyon
4. Modern RLWTF releases: effluent collected 8/2009
5. Naturally occurring background nitrate: measured in uncontaminated wells on Pajarito Plateau; recast into a probability distribution

Nitrate in both intermediate and alluvial wells has generally more negative $\delta^{15}N$ and more positive $\delta^{18}O$ values, which can not be explained by mixing with current effluent sources in Mortandad Canyon. This suggests chemical treatment processes at the RLWTF have changed.



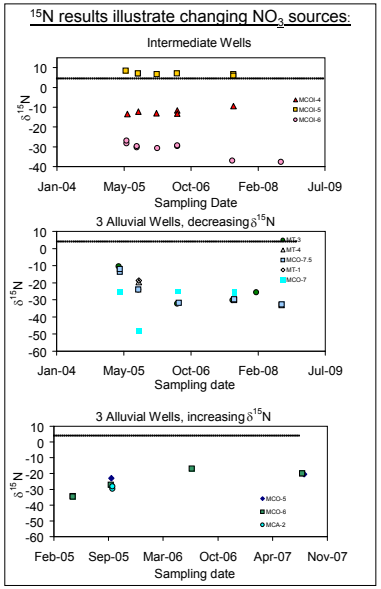
Background Subtraction for Mixing Proportions

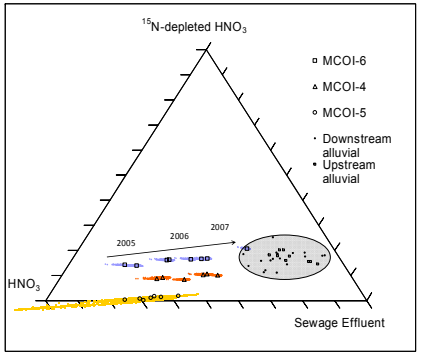
Recast mixing among 4 sources into 3 anthropogenic components by subtracting background to get 3-component system
NO_3(total) = NO_3(background) + NO_3(contaminant)

$$\delta^{15}N_A \cdot X_A + \delta^{15}N_B \cdot X_B + \delta^{15}N_C \cdot X_C = \delta^{15}N_{corrected}$$
$$\delta^{18}O_A \cdot X_A + \delta^{18}O_B \cdot X_B + \delta^{18}O_C \cdot X_C = \delta^{18}O_{corrected}$$

As defined by mass balance relationships, groundwater samples that have lower nitrate concentration are most affected by the background correction calculation. This relationship also demonstrates the importance and uncertainty that develops when choosing end member nitrate concentrations and isotopic values.

^{15}N results illustrate changing NO_3 sources:

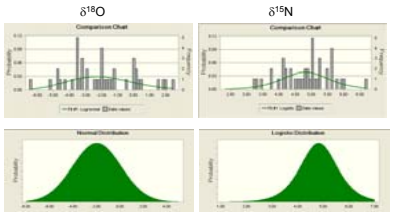




Intermediate wells: $\delta^{15}N$ decreases (except in MCOI-4). In terms of mixing components, all trend toward a mixed source of 80% sewage effluent, 20% ^{15}N-depleted nitric acid.

Alluvial wells: trend toward more positive $\delta^{15}N$ values, showing the bulk of the isotopically light anthropogenic plume has passed through area, to the downcanyon wells.

Probability Distribution of Background & Error Analysis



Using measured values and associated physical limits, a theoretical distribution of 500 random possible combinations of background nitrate concentration, $\delta^{15}N$ and $\delta^{18}O$ 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. This set of 500 random background nitrate values is used in the previously described background subtraction calculation to generate, in a probabilistic fashion, background-corrected stable isotope ratios for each sample.

Conclusions

- Chemical processing imparts distinct N and O isotope signatures that are preserved for years in aerobic groundwater systems.
- Downgradient alluvial wells show decreasing nitrate concentrations, and a smaller 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 MCOI-5. Unexpected sewage contaminant source in MCOI-6. 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 probabalistic 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 chemicals used during processing could confound apparent trends. This would be difficult to interpret in a mixed-source environment, without knowledge of other geochemical parameters.
- Downgradient groundwaters have the potential to preserve stable isotope signatures of chemical processing.
- Future work:
  - better understand isotopic variations in other anthropogenic sources at LANL, and historic variability.
  - mechanism of formation and variability in background nitrate
  - improve detection limits/precision, and analyze nitrite in anaerobic waters

Acknowledgments

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