Isotopic Composition of Natural Nitrate at the Los Alamos National Laboratory in North Central New Mexico, USA

Abbey E. Chrystal[1], Jeffrey M. Heikoop[1], Patrick Longmire[1], Michael Dale[2], Toti Erik Larson[1], George Perkins[1], June Fabryka-Martin[1], Ardyth M. Simmons[3], Julianna Fessenden-Rahn[1]

1)Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM, USA.

2) New Mexico Environment Department, Department of Energy Oversight Bureau, Los Alamos, NM, USA.

3) Los Alamos National Laboratory Water Stewardship Program, Los Alamos National Laboratory, Los Alamos, NM, USA.

Introduction

• In addition to natural background there are three known anthropogenic sources of groundwater nitrate (NO_3^-) at Los Alamos National Laboratory (LANL).

• Stable isotopes of nitrogen and oxygen can help to distinguish among these sources, define groundwater flow paths and evaluate groundwater mixing.

• Error analysis of the background data set reveals a probability distribution of possible values.

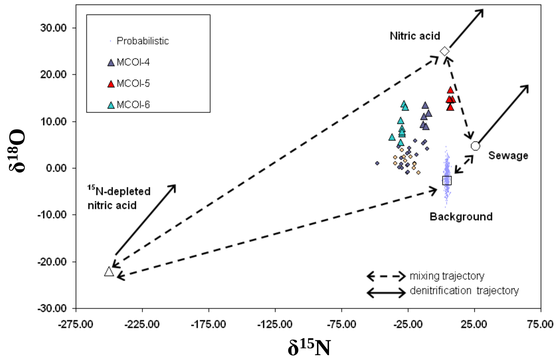


Figure 1: Four sources of NO_3^- with distinct $\delta^{15}N$ and $\delta^{18}O$ compositions are present in Mortandad Canyon (LANL) groundwater within the alluvium and perched intermediate-depth aquifers. From Larson et al (in preparation).

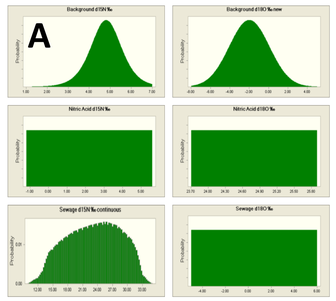
Conclusions

• Probabilistic analyses allow for more rigorous differentiation between natural and anthropogenic sources of NO_3^-,.

• There may be a mechanism that allows for elevated concentrations of natural NO_3^- while retaining natural NO_3^- isotopic signature in groundwater.

• Background NO_3^- UTL's may need to be redefined in context of both concentration and isotopic composition.

1. Given the background distribution, what is the probability that some component of contamination could still be present?



For δ15N = 5.02 and δ18O = -1.21			
Percentile	Background	Nitric Acid	Sewage
0%	0.6	0.05	0
10%	0.68	0.1	0.01
20%	0.72	0.12	0.02
30%	0.74	0.14	0.03
40%	0.77	0.16	0.04
50%	0.79	0.18	0.05
60%	0.81	0.2	0.06
70%	0.84	0.21	0.07
80%	0.87	0.23	0.09
90%	0.91	0.05	0.12
100%	1.05	0.1	Infinity

B

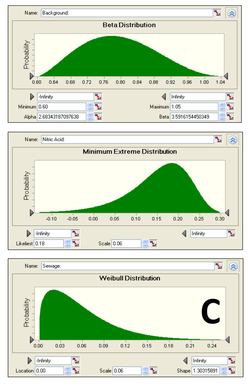


Figure 2: A) Assigned distributions created for background, nitric acid and sewage based on samples and literature review. B) Probabilistic composition results for a random sample within the background distribution. (Crystal Ball software) C) Probabilistic percent composition distributions for a random sample within the background distribution (Crystal Ball software).

•Generate 2000 sample points within the distribution using latin hypercube sampling (LHS).

•Solve linear equations for each new sample point to determine probabilities of percent composition.

•Example: for a sample with $\delta^{15}N$=5.02 and $\delta^{18}O$=-1.21, there is a 90% chance that the sample contains <5% nitric acid and <12% sewage (Fig 2B)

2. LANL NO_3^- background is defined by concentration (UTL=0.3 mg/L as N) but isotopes and concentration are not correlated.

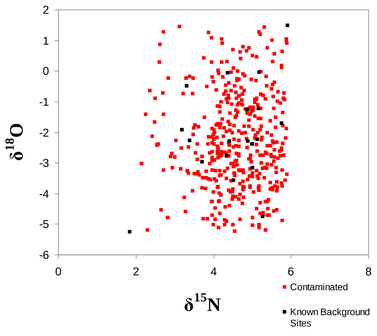


Figure 3 $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in known background sites (black) and of all measured sites (red), for the full range of isotopic values measured for background sites.

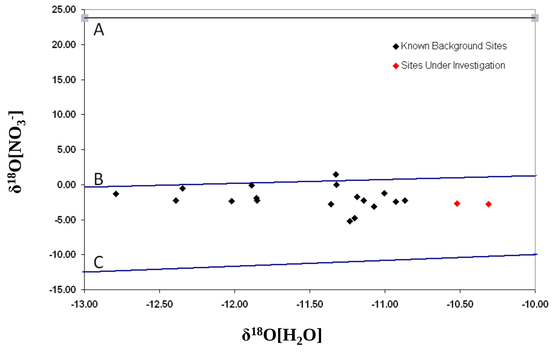


Figure 4: After McMahon and Bohlke (2006). $\delta^{18}O$ of groundwater ($\delta^{18}O$ [H_2O]) and $\delta^{18}O$ of nitrate ($\delta^{18}O[NO_3^-]$). Black dots represent known background sites. Red dots represent two of the sites that are considered contaminated with respect to NO_3^- concentration, but that fall within the range of background values for $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-. Lines represent hypothetical relationships of:
A) $\delta^{18}O[NO_3^-]$= $\delta^{18}O$ [atmospheric O2]
B) $\delta^{18}O[NO_3^-]$=2/3 $\delta^{18}O$ [H_2O]+ 1/3 $\delta^{18}O$ [atmospheric O2] and
C) $\delta^{18}O[NO_3^-]$= $\delta^{18}O$ [H_2O]

•Many sites that are considered contaminated with respect to NO_3^- concentration are isotopically similar to known background sites.

•$\delta^{18}O$ plots as expected just below line B (Fig.5) representing nitrification in the vadose zone prior to recharge (*McMahon and Böhlke 2006*).

•$\delta^{18}O[H_2O]$ indicates that there are differences in groundwater isotopes that could be related to precipitation.

Next Steps

•What mechanism could produce elevated natural nitrate?

- •Geologic source unlikely
- •NO_3^- can accumulate in soil in arid environments.
- • Geospatial analysis of groundwater ages, water table geology and flow paths, recharge and paleoclimate data may provide insight.

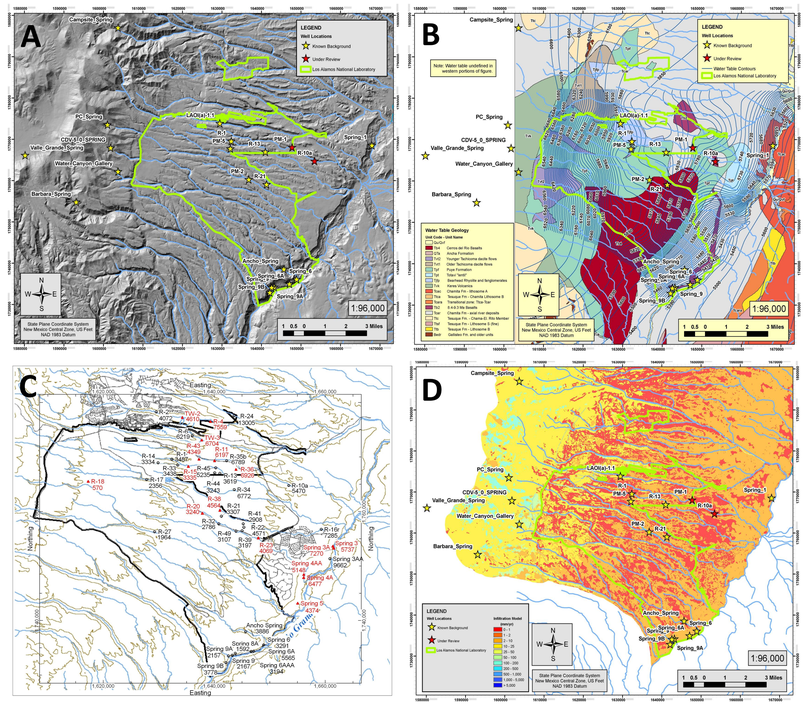


Figure 5: A) Well and Spring locations in the vicinity of LANL. Yellow stars represent sites considered to be background with respect to nitrate. Red stars are examples of sites that are considered to be contaminated due to elevated nitrate concentrations though they share isotopic signatures of the background sites. B) Water table geology and elevation. C) Uncorrected ^{14}C ages for LANL waters . D) Infiltration.

LA-UR 09-08027