Sourcing Vadose Zone and Groundwater Nitrate Using Nitrate Isotopes

Katharine Woods, Michael Singleton, Mark Conrad, and Donald DePaolo
Contact: Katharine Woods, 510/486-5659, knwoods@lbl.gov

RESEARCH OBJECTIVES

Nitrate is one of the of the most widespread groundwater contaminants in the United States. There are a number of potential sources for nitrate contamination, including fertilizers, chemical processing, sewage, and elevated natural backgrounds. Analyses of the nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) isotope ratios of the nitrate represent a powerful tool for distinguishing between different sources. Methods for analyzing the $\delta^{15}N$ and $\delta^{18}O$ values of dissolved nitrate have historically been unwieldy and time-consuming. However, recent advances using denitrifying bacteria to generate N_2O from nitrate have greatly reduced both the preparation time and sample size requirements.

We have streamlined this denitrification technique and are using it for research on the fate and transport of nitrate in the vadose zone. To date, we have applied this technique to tracking nitrate contamination associated with radioactive waste at the Hanford site in south-central Washington and identifying the sources of nitrate in the Exploratory Studies Facility at Yucca Mountain. Highlights of the work at Hanford are presented below.

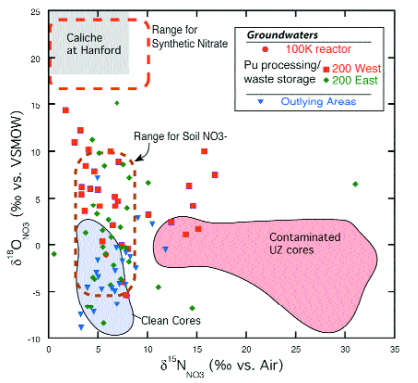

Figure 1. Plot of nitrogen versus oxygen isotope ratios of groundwater nitrate from the Hanford site in south-central Washington. Also shown is the range of values measured for unsaturated zone nitrate from clean and contaminated core samples from Hanford, and the general ranges of isotopic compositions of soil nitrate and synthetic nitric acid.

APPROACH

We modified the existing bacterial technique by increasing initial culture inoculation. We also grow the cultures on the bench top in vials used for our automated headspace sampler and reduced the venting time of the vials before injecting the sample, to decrease sample-processing time. Groundwater samples from the Hanford site were injected directly into inoculated vials. Vadose zone nitrate was extracted from cores by rinsing dried sediment with de-ionized water. The filtered rinse water, assumed to contain the nitrate originally dissolved in the pore fluids, was then injected into the inoculated vials. The vials are then loaded into the headspace sampler and analyzed using an automated trace gas pre-concentration system interfaced to a continuous-flow isotope-ratio mass spectrometer (CF-IRMS).

ACCOMPLISHMENTS

The modifications to the bacterial nitrate technique have significantly reduced sample preparation time. The use of the automated headspace sampler coupled to the CF-IRMS system has also reduced the amount of nitrate necessary per analysis. Using this method, we are able to analyze samples with nitrate concentrations as low as 0.2 mg/L. The reproducibility of the method is ±0.2‰ for $\delta^{15}N$ and ±0.3‰ for $\delta^{18}O$ (1σ).

The method has been successfully used to identify the sources of vadose zone nitrate at the Hanford site. The relationships between the vadose zone nitrate and nitrate contamination in the groundwater are summarized below.

SIGNIFICANCE OF FINDINGS

The isotopic compositions of nitrate in unsaturated zone (UZ) and groundwater samples from Hanford indicate at least four potential sources of nitrate in the groundwater. Natural sources of nitrate include microbially produced nitrate from the soil column ($\delta^{15}N$ of 4 to 8‰, $\delta^{18}O$ of -9 to 2‰) and nitrate in buried caliche layers ($\delta^{15}N$ of 0 to 8‰, $\delta^{18}O$ of -6 to 42‰). Industrial sources of nitrate include nitric acid in low-level wastewater ($\delta^{15}N$ ~0‰, $\delta^{18}O$ ~23‰) and nitrate in high-level radioactive waste from plutonium processing ($\delta^{15}N$ of 8 to 33‰, $\delta^{18}O$ of -9 to 7‰). The isotopic compositions of nitrate in 97 groundwater wells with nitrate concentrations up to 1,290 mg/L have been analyzed (Figure 1). These data indicate that the primary sources of nitrate in groundwater are nitric acid and natural nitrate flushed out of the UZ during disposal of low-level wastewater. Nitrate associated with high-level radioactive UZ contamination does not appear to be a major source of groundwater nitrate.

RELATED PUBLICATION

Singleton, M.J., K.N. Woods, M.E. Conrad, D.J. DePaolo, and P.E. Dresel, Tracking sources of unsaturated zone and groundwater nitrate contamination using nitrogen and oxygen stable isotopes at the Hanford Site, Washington. Environ. Sci. Technol., 39, 3563–3570, 2005. Berkeley Lab Report LBNL-57044.

ACKNOWLEDGMENTS

Funding for this study was provided by the Department of Energy under Contract DE-AC06-76RL01830, through the Hanford Science and Technology Program, and by the Assistant Secretary for Environmental Management, Office of Science and Technology, under the Environmental Management Science Program of the U.S. Department of Energy under Contract DE-AC03-76SF00098.