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Tracking sources of unsaturated zone and groundwater nitrate contamination using stable isotopes

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Abstract

The nitrogen and oxygen isotopic compositions of nitrate in pore water extracts from unsaturated zone (UZ) core samples and groundwater samples indicate at least four potential sources of nitrate plumes in groundwaters at the USDOE Hanford Site in south-central Washington. These nitrate sources are 1) microbially produced nitrate from the soil column (δ^{15}N of 4 to 8‰, δ^{18}O of -9 to 2‰), 2) nitrate in buried caliche layers (δ^{15}N of 0 to 8‰, δ^{18}O of -6 to 42‰), 3) nitric acid in low-level disposal waters (δ^{15}N ≈ 0‰, δ^{18}O ≈ 23‰), and 4) co-contaminant nitrate in high-level radioactive waste from plutonium processing (δ^{15}N of 8 to 33‰, δ^{18}O of –9 to 7‰). The isotopic compositions of nitrate have been analyzed from 91 groundwater wells with concentrations up to 763 mg/L NO₃⁻. Estimates based on isotopic mixing indicate that even the wells with the highest nitrate concentrations contain at least 30% of nitrate from natural sources in the UZ. These data indicate that major nitrate plumes resulted from flushing nitrate out of the UZ during disposal of low-level wastewater and nitric acid, rather than migration of the nitrate associated with high-level radioactive UZ contamination.

Introduction

Nitrate is the most abundant anion reported in contaminated groundwater, soils, and sediment at USDOE facilities (1). A considerable mass of nitrate may accumulate by natural processes in the UZ in arid and semi-arid climates, where infiltration of water at the surface is low (2). Groundwater quality may be significantly impacted when this sink of nitrate is mobilized by activities that enhance natural infiltration to the UZ such as irrigation, storage of water in aquifers, or wastewater disposal in infiltration ponds. The
The dual isotopic composition of nitrate (δ^{15}N and δ^{18}O) can be used as a tracer for industrial and natural sources, and can give valuable insight into transport through unsaturated zone and groundwater systems. However, few studies have examined the processes that affect the isotopic composition of nitrate in contaminated industrial settings (e.g., 3, 4).

The isotopic composition of nitrate has been documented throughout diverse ecosystems (5-10). The cycling of nitrate in soils is complex, with inputs from precipitation, surface water, and possibly contamination combined with numerous co-occurring microbial processes. Soil microbes tend to favor uptake of the lighter isotopes of N and O, leaving the residuum enriched in the heavier isotopes. For example, the process of denitrification (microbially-mediated reduction of nitrate to N_{2}) results in a trend of higher values (both for δ^{15}N and δ^{18}O), and has been of particular interest to groundwater and surface water studies (3-6, 11).

Recent interest in the bioremediation of uranium has led to the realization that nitrate, which is commonly associated with uranium in industrial contamination, strongly affects the mobility of uranium by inhibiting the ability of metal reducing bacteria to convert the soluble U(VI) to the insoluble U(IV) (12). Bioremediation efforts therefore require a detailed understanding of local sources of nitrate, as well as abiotic and biological processes affecting nitrate in industrial settings.

Our investigation of nitrate at the Hanford Site uses borehole sediment samples to determine sources of nitrate in the UZ. Potential industrial sources of nitrate in the UZ are evaluated based on sediment samples from two boreholes through radionuclide-contaminated sediments at high-level waste tank farms. Natural sources of nitrate are determined from two boreholes in relatively undisturbed areas. The isotopic
compositions of UZ nitrate sources are then compared with nitrate from the local unconfined aquifer to determine the sources of groundwater contamination. Measurements of the nitrogen and oxygen isotopic compositions of nitrate provide a promising method to identify sources and track the transport of co-contaminant nitrate and associated radioactive contaminants from the UZ into groundwater.

Site Description. The Hanford Site is located in the Pasco Basin in south-central Washington, USA (Figure 1). The Pasco Basin consists of mostly unconsolidated sedimentary deposits overlying gently folded and faulted Miocene tholeiitic basalt flows of the Columbia River Basalt Group. The unsaturated zone is generally 50-70m thick and overlies a 40-180 m thick unconfined aquifer that flows from west to east across the site. Both the unsaturated zone and unconfined aquifer are hosted in the gravel silts and clay of the fluvial Pliocene Ringold Formation and the Pleistocene flood deposits known locally as the Hanford Formation. A “caliche” zone of pedogenic carbonate, part of the Cold Creek Unit (CCU), was developed on top of the eroded surface of the Ringold Formation and in overlying gravel deposits during arid climate conditions (13, 14).

Nitrogen-bearing chemicals were used extensively in plutonium extraction and purification processes carried out at the Hanford Site. Nitrate concentrations >2000 mg/L have been reported for Hanford groundwaters (15), where nitrate commonly accompanies radionuclide contamination. High levels of nitrate in drinking waters can lead to health problems such as “blue baby” syndrome, and the USEPA has established a maximum contaminant limit (MCL) of 45 mg/L (as NO₃⁻) in drinking waters (16). Many wells at the Hanford Site exceed the drinking water standard for nitrate, although currently no remediation of the nitrate contamination is occurring or anticipated. Nonetheless, it is
critical to understand the source and transport of nitrate at Hanford because nitrate is intimately linked with the sources and processes affecting radioactive contaminants.

Figure 1. Location of the Hanford Site and 200 Areas where cores were collected in contaminated areas near two tank farms and in two areas with no known contamination. Contours are shown for nitrate concentrations in the Hanford unconfined aquifer (simplified after 15). Groundwater samples from 91 wells have been analyzed for nitrate isotopic composition (dots). Nitrate concentrations in these wells range from 1.5 to 763 mg/L (15).
Analytical Procedure.

For the pore water extracts, 30 g of sediment were combined with 30 ml of 18MΩ de-ionized water, shaken for 90 minutes at room temperature and allowed to stand for 24 hours. The nitrate contained in the rinse water is assumed to be that which was originally dissolved in the pore fluid. After 24 hours, the leach solutions were vacuum filtered through a 0.45 µm polyethylene filter into sealed glass vials and kept cool and dark until analysis.

Until recently, methods for analyzing δ^{15}N and δ^{18}O of dissolved nitrate were unwieldy for routine analyses of dilute groundwaters and (small volume) pore water extracts from unsaturated zone sediments. A recently developed method uses denitrifying bacteria to generate N_{2}O from NO_{3}^{-} and NO_{2}^{-} in dilute and saline samples (17, 18). This method allows for simultaneous δ^{18}O and δ^{15}N analyses on low concentration samples (down to 0.5 mg/L NO_{3}^{-}) and low sample volume (< 4 mL). The bacterial denitrification process consumes both nitrate and nitrite, which can complicate the interpretation of the results. This is not a problem for the samples studied here because they contain very little nitrite. We refer to analyses in the following sections as representing the isotopic composition of nitrate, with the understanding that the results may also reflect a minor contribution by any nitrite that may be present.

The processing of nitrates for simultaneous δ^{15}N and δ^{18}O measurements at the Center for Isotope Geochemistry at Lawrence Berkeley National Laboratory is conducted using a modified version of the original denitrifying bacteria procedure (17, 18). The method has been adapted to decrease the time required for culture preparation and sample processing (19). Cultures of *Pseudomonas chlororaphi* (American Type Culture
Collection strain #13985, previously classified as *P. aureofaciens*) are grown in a Tryptic soy broth at room temperature, and are agitated 2-3x daily by inversion, for two days. The *P. chlororaphis* bacteria are nitrate reducers with a truncated pathway; they metabolize the nitrate in the samples and produce N₂O as their metabolic waste instead of carrying the process all the way to N₂. Cultures are divided and centrifuged to extract the cells from the medium. The pellets of cells are re-suspended in headspace vials with small amounts of spent medium to produce highly concentrated cultures. The concentration of cells varies by concentration of sample to be run. Vials are sealed, and helium is bubbled through the reaction culture for 15 min to flush out any N₂O in the vial.

Samples and standards for the run are injected (10 µL to 4mL depending on NO₃⁻ concentration) into the vials with the re-suspended culture and left overnight. The following morning, 0.1 mL of 12N NaOH is injected into the vials to kill the cells, stop the reaction, and draw down any CO₂. Vials are then placed on an automated headspace sampler, and the N₂O is processed through a GV Instruments (Manchester, UK) Tracegas pre-concentrator unit. After cryo-focusing and separation from CO₂, the N₂O is then passed into an IsoPrime continuous flow mass spectrometer for measurement of the isotope ratios. Isotopic values are corrected to KNO₃ standards USGS32, USGS34, USGS35, and IAEA-N3 using the values determined by (20). The standard salts are dissolved in DI water from the same source used for soil leaches, which has a δ¹⁸O value of –13‰, and is within 4 ‰ of typical Hanford Site groundwater and UZ pore water. Values of δ¹⁵N are reported relative to N₂ in air, and δ¹⁸O values are reported relative to Standard Mean Ocean Water (SMOW). Blanks are run with each set, and are typically below detection limit (<0.5 mg/L NO₃⁻).
Results and Discussion

Background Nitrate. The isotopic composition of nitrate formed by microbial nitrification in soils produces a recognizable oxygen isotopic composition, where

$$\delta^{18}O_{NO_3} = \frac{2}{3} \delta^{18}O_{H_2O} + \frac{1}{3} \delta^{18}O_{O_2}. $$

This relation results from microbes deriving 1 atom of O from the atmosphere and 2 atoms from the local pore water during nitrate production (5). On average, UZ pore water at the Hanford Site has a $\delta^{18}O$ value of –15 ‰ (21), and the $\delta^{18}O$ value of O$_2$ in air is 23 ‰ (22). Therefore, microbe-mediated nitrate production at Hanford would have a predicted $\delta^{18}O$ value of around –2 ‰. The nitrogen in microbially produced nitrate is derived from N species in the soil (e.g., NH$_4$, NO$_2$, N$_2$O) or N$_2$ from the atmosphere, and typically has a $\delta^{15}N$ value that is slightly on the positive side of zero.

Pore water concentrations of nitrate range from 26 to 507 mg/L (23) in “clean” UZ sediments from borehole BG1, which has no indication of radioactive contamination (Figure 1; now the location of well 299-W22-48). The highest concentrations of nitrate in BG1 occur in the caliche of the CCU from 44.5 to 45.4 m depth (23). Pore water nitrate in BG1 samples has $\delta^{15}N$ values that range from 5 to 12 ‰ and $\delta^{18}O$ values from –9 to 4 ‰ (Figure 2). Such isotopic compositions are broadly consistent with microbially mediated production of nitrate at the surface. Both the $\delta^{18}O$ and $\delta^{15}N$ of nitrate in BG1 pore water indicate two disturbances at depth (18 m and 45 m) possibly due to lateral flow of non-radioactive wastewater. Disturbances in the $\delta^{18}O$ values of pore water are reported for this core, and were attributed to lateral migration from waters disposed nearby (21).
Figure 2. Pore water nitrate $\delta^{15}$N and $\delta^{18}$O values in “clean” unsaturated zone sediments from borehole BG1 in the 200 West Area. Pore water concentrations of nitrate in BG1 sediments range from 75 to 507 mg/L (23).

Uncontaminated sediments in borehole BG2 (Figure 1; now the site of well 299-E17-22) have nitrate $\delta^{15}$N values that range from 4 to 5 ‰ and $\delta^{18}$O values from –5 to 2 ‰ (Figure 3). Nitrate $\delta^{15}$N values in BG2 show little variation with depth. The lack of variation suggests that this vertical profile has not been impacted by lateral migration of wastewater discharge.

The $\delta^{18}$O values of nitrate in both BG1 and BG2 show minor variation with depth. Excluding the samples in BG1 at 18m and 45m depths, the variations in nitrate $\delta^{18}$O from the two clean cores range from –9 to 2 ‰. These variations may be related to local pore
water isotopic compositions when the nitrate was originally produced. The semi-arid climate of Hanford leads to seasonal shifts of 3 to 12 ‰ in pore waters within a few meters below the surface (24). For example, the water is likely to vary in δ¹⁸O from –17 to about –5 ‰. Hence, if nitrate is produced from these waters, it would be expected to have a δ¹⁸O value of –4 to +4 ‰. This predicted range corresponds well with the measured values in BG2. Some samples from BG1 have a somewhat lower δ¹⁸O value. The variation in pore water δ¹⁸O values may result in microbially produced nitrate that acquires different values of δ¹⁸O depending on the season in which it is produced.

Figure 3. Pore water nitrate δ¹⁵N and δ¹⁸O values in “clean” unsaturated zone sediments of borehole BG2 in the 200 East Area.
Buried caliche layers (CCU) in the Hanford unsaturated zone tend to have nitrate concentrations that are an order of magnitude higher than pore water nitrate in other units. Nitrate in DI leaches of three outcrop samples believed to be stratigraphically equivalent to the buried CCU carbonates (14) have δ^{15}N values of 0 to 8‰ and δ^{18}O of 18 to 42‰. A sample of buried caliche from archived core collected in the 200W area has a nitrate δ^{15}N value of -3 ‰ and a δ^{18}O value of 37 ‰. The caliche nitrate δ^{15}N values overlap the microbially produced nitrate values, but the δ^{18}O values of most caliche nitrate samples are much higher than those of the microbial nitrate. This relation is consistent with the isotopic compositions reported for nitrate in desert evaporite deposits (25), and likely represents long-term deposition of atmospheric nitrate prior to burial. One exception is nitrate from the caliche at 45m depth in BG1, which has an isotopic composition consistent with microbial nitrification.

**Contaminated Cores.** The tank farm borehole TF1 (core # C3832) was drilled during May of 2002 near the TX-104 tank in the 200 West area of the Hanford Site (Figure 1). Samples collected from TF1 between depths of 19m and 34m had high U concentrations ranging from 3-35 mg/L (26). Above this zone of contamination, pore water has nitrate concentrations of 7-62 mg/L, however in the contaminant zone nitrate concentrations increase to 131-883 mg/L (26). Nitrate in pore water above the contaminated zone in TF1 has δ^{15}N values from 6 to 10 ‰ and δ^{18}O values from -1 to 20 ‰ (Figure 4). Within the contaminated zone, δ^{15}N values of nitrate increase to between 8 and 16 ‰, and the nitrate δ^{18}O values range from -2 to 7 ‰.
Figure 4. Pore water nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in core TF1, located in contaminated sediments near tank TX104 in the 200 West Area.

Samples from tank farm borehole TF2 (core # C4105) were collected from January to March, 2004 near waste tank T-106 in the 200 West area (approximately 600 m north of TF1; Figure 1). Samples from TF2 showed high levels of $^{99}\text{Tc}$, $^{60}\text{Co}$, and $^{101}\text{Ru}$ at depths between 14 and 40 m (27). Pore water nitrate in TF2 is generally 50 to 200 mg/L within 15 m of the surface, but increases to between 2000 and 8000 mg/L within the zone of contamination. Two samples taken above the contaminant zone in TF2 have $\delta^{15}\text{N}$ values of 4 and 6 ‰ and $\delta^{18}\text{O}$ values of 9 and 20 ‰ (Figure 5). Within the zone of radionuclide contamination, the elevation in nitrate concentration coincides with a shift in isotopic composition of nitrate to $\delta^{15}\text{N}$ values that range from 19 to 33 ‰ and $\delta^{18}\text{O}$ values of –9 to 2 ‰.
Figure 5. Pore water nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in core TF2, located in contaminated sediments near tank T106 in the 200 West Area.

Nitrate concentrations are relatively low above the contaminated zones in both TF1 and TF2. The upper 12m in each borehole consists of coarse sand and gravel fill, which was used to bury the waste tanks. One sample at 14m depth in TF1, may show a trace of the high $\delta^{15}\text{N}$, low $\delta^{18}\text{O}$ nitrate that is abundant in the deeper contaminated sediments. However, most samples collected from the shallow, uncontaminated sediments have $\delta^{15}\text{N}$ values of 4 to 6 ‰ and $\delta^{18}\text{O}$ values from 9 to 20 ‰. Such values are consistent with the deposition of atmospheric nitrate or a synthetic nitrate such as HNO$_3$. The source for nitrogen in most commercially produced chemicals is atmospheric N$_2$, which is also the reference gas used for $\delta^{15}\text{N}$ measurements. Hence, the $\delta^{15}\text{N}$ values expected for chemical sources of nitrate are close or slightly higher than 0‰ (28). The
$\delta^{18}O$ values of chemical sources of nitrate are close to 23‰ (28), the value of atmospheric $O_2$ (22).

Figure 6. $\delta^{15}N$ and $\delta^{18}O$ values for porewater nitrate from unsaturated zone boreholes at the Hanford Site. For clarity, samples from non-contaminated fill in the upper 15 m of TF1 and TF2 are not shown. Ranges reported for soil nitrate and synthetic nitrate (5, 28) are shown for reference.

Samples from the contaminated sediments of TF1 and TF2 have unusually high $\delta^{15}N$ values, which may indicate a unique signature for nitrate associated with high-level waste at Hanford (Figure 6). The isotopic composition of nitrate present in high-level radioactive wastes at Hanford may have been altered by processes occurring in the plutonium extraction and purification process, during storage, or after it leaked into the soil. The oxygen and nitrogen isotopic signature of this nitrate is inconsistent with processes such as denitrification that result in a shift of both the $\delta^{15}N$ and $\delta^{18}O$ to higher
values (3, 5). Likewise, loss from volatilization of NO\textsubscript{x} during fuel rod dissolution or evaporation of waste during volume reduction processes would likely lead to a high $\delta^{15}\text{N}$ and high $\delta^{18}\text{O}$ nitrate in the waste. Instead, the isotopic composition of nitrate in UZ tank farm contamination indicates that the fractionation processes were not coupled between N and O, leading to nitrate with high $\delta^{15}\text{N}$ values but low $\delta^{18}\text{O}$ values.

The decoupled N and O isotopic compositions can be explained if ammonia played a role in the nitrate chemistry of the tank waste. Ammonia forms in the high-level waste through a variety of processes including reaction of NaNO\textsubscript{3} and NaOH used in dissolution of Al cladding around fuel rods, decomposition of sulfamate (SO\textsubscript{3}NH\textsubscript{2}) used for Plutonium reduction with nitrite, and by radiolysis of nitrate and nitrite (29). An enrichment in the $^{15}\text{N}$ content of ammonia during or after one of these processes followed by oxidation to nitrate in the presence of process water ($\delta^{18}\text{O} \approx -17 \%$) or deep pore water ($\delta^{18}\text{O} \approx -15 \%$) could produce the observed nitrate with high $\delta^{15}\text{N}$ and low $\delta^{18}\text{O}$ values. This process would require large-scale oxidation of ammonia in order to explain the high concentrations of nitrate associated with the high-level contaminants. Extensive groundwater monitoring has not found any significant presence of ammonia in Hanford groundwaters (15), suggesting that any ammonia present in the UZ is oxidized before reaching the water table.

The increase of $\delta^{15}\text{N}$ values due to NO\textsubscript{x} loss during metal cladding dissolution followed by re-equilibration with low $\delta^{18}\text{O}$ water provides an alternative process that may have resulted in the peculiar isotopic composition of co-contaminant nitrate near the tank farms. At neutral pH, the $\delta^{18}\text{O}$ of nitrate is slow to re-equilibrate with oxygen in its solvent water, even at near boiling temperatures. However, the $\delta^{18}\text{O}$ of nitric acid is
susceptible to isotopic exchange with water oxygen on time scales of a few hours or days (depending on temperature), as can be demonstrated when making nitrate reference salts by mixing waters of a desired $\delta^{18}O$ value with concentrated HNO$_3$ (20). A similar isotopic exchange may have occurred in the high level waste at Hanford, after fractionation by NO$_x$ loss during the acid dissolution of metal cladding around the fuel rods, which would have enriched the nitrate in heavy nitrogen and oxygen isotopes. When the wastes came into contact with process water, the $\delta^{18}O$ may have been reset by isotopic exchange with the water oxygen, while the $\delta^{15}N$ remained high. This process most likely took place during the chemical processing, since a high pH was maintained in waste storage tanks to prevent corrosion. Bench-top scale experiments are needed to test these hypotheses and to better define plausible processes that could lead to the unique signature of co-contaminant nitrate. Regardless of its cause, this unique isotopic signature provides a valuable tracer for nitrate associated with high-level radioactive contaminants at Hanford.

**Groundwater.** Groundwater samples from 91 wells at Hanford (Figure 1) have been analyzed for nitrate $\delta^{15}N$ and $\delta^{18}O$ values (Figure 7). Nitrate concentrations in these wells range from 1.5 to 763 mg/L (15). In areas outside the chemical processing facilities, most samples of groundwater nitrate have isotopic compositions similar to natural microbially produced nitrate. The isotopic composition of nitrate plumes in the chemical processing facilities (200 Areas) are consistent with a mixture of nitrate from microbial nitrification with nitrate that has high $\delta^{18}O$ values, such as synthetic nitrate (e.g., nitric acid) or nitrate from the caliche layers present in the Hanford unsaturated
zone. Our collection of groundwater samples has only indicated four wells with nitrate isotopic compositions that lie within the high δ¹⁵N, low δ¹⁸O field of UZ pore fluids contaminated with high-level radioactive waste. Three of these wells are located directly adjacent to tank farms (S-SX, T, and A-AX). The fourth well is located close to the Columbia River, but outside of any areas known to contain high level waste. It is possible that denitrification could shift some of the background samples to correspond to some of the lower δ¹⁵N samples of co-contaminant nitrate. However, the data collected so far does not indicate that denitrification has a strong influence on δ¹⁵N or δ¹⁸O values of groundwater nitrate at Hanford, most likely due to the prevalence of oxidizing conditions.

Figure 7. δ¹⁵N and δ¹⁸O values of nitrate in groundwater at the Hanford Site. The isotopic compositions of nitrate in clean and contaminated sediments from this study and ranges reported for soil nitrate and synthetic nitrate (5, 28) are shown for reference.
Nitric acid was commonly disposed along with low-level contaminated wastewater that was dumped in cribs, trenches, and ponds (30). The isotopic composition of nitrate associated with caliche overlaps with the composition expected for nitric acid, but microbially produced nitrate has a much different δ^{18}O value than nitric acid or atmospheric deposited nitrate in the caliche. It is therefore possible to use a simple mixing model to estimate the minimum amount of nitrate from natural sources in the groundwater samples based on their δ^{18}O values. Using the previously discussed δ^{18}O values of −2‰ for soil nitrate and 23‰ for nitric acid, and neglecting any input from caliche nitrate indicates that between 30% and 100% of the nitrate in groundwater samples from the chemical processing areas was derived from the ambient soil column. The minimum contribution from natural soil nitrate would increase for samples that were affected by (higher δ^{18}O) nitrate from buried caliche layers. Considering that nitrate concentrations from these groundwater samples are as high as 763 mg/L, this indicates that a significant amount of nitrate was mobilized from natural sources in the UZ.

Low pre-industrial infiltration rates and the presence of buried caliche layers provide a considerable mass of nitrate in the Hanford UZ. These reservoirs of nitrate in the UZ may have been disturbed by the approximately 10^8 m^3 of dilute wastewater that were discharged to surface disposal facilities in the chemical processing areas (31). Isotopic data from groundwater nitrate indicates that both natural and industrial sources contributed to the major nitrate plumes in groundwater below Hanford chemical processing facilities. However, the migration of nitrate associated with high-level radioactive UZ contamination does not appear to be a cause of nitrate plumes currently present in Hanford groundwater.
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