

Project Title: **Isotopic Tracers for Waste Fluid Tracking and Fluid-Soil Interactions: Hanford, Washington**

Project Number: **73773**

Lead PI: **Dr. Donald J. DePaolo, Lawrence Berkeley National Laboratory**

RESEARCH OBJECTIVE

The objective of this research is to develop and advance isotopic methods for characterizing fluid flow and chemical transport through the vadose zone to groundwater. Previous research has been concentrated on developing and comparing different isotopic systems (e.g., hydrogen, oxygen and strontium isotopes) for determining fluid infiltration rates and pathways in the vadose zone (e.g., Maher et al., 2003; DePaolo et al., 2004; Singleton et al., in press). The focus of our current efforts is on using the isotopic compositions of different chemical phases (e.g., uranium, nitrate) to track their movement through the vadose zone. Preliminary results indicate that this will be a powerful tool for assessing environmental risks associated with vadose zone contamination.

RESEARCH PROGRESS AND IMPLICATIONS (for second year of three-year renewal project)

SUMMARY HIGHLIGHTS

- The flux of contaminant uranium from Hanford to the Columbia River is estimated to be up to 2-3 kg/day, varying seasonally.
- A component of Hanford U can be identified 350 km down river.
- The nitrogen and oxygen isotopic compositions of groundwater nitrate can be used to distinguish high-level radioactive waste from low-level process waste.

Tracking Uranium Contamination in the Columbia River • In the first year report, we described the initial results of a study of the flux of contaminant uranium from the Hanford Site to the Columbia River. We have now analyzed additional river water traverses collected during the spring of 2004 at 0.5 km south of the 300 Area, at the Vernita Bridge, and at the Richland Pump House. Our earlier traverse was limited to samples collected from about half depth of the river, thus missing any vertical structure in the contaminant plume. The spring 2004 traverses included depth profiles at each of the sampling stations. The Richland was coordinated with an ADCP (acoustic Doppler current profiler) to provide velocity and flow profiles. We also analyzed samples from agricultural return canals along the east bank of the Columbia, 300 Area wells and seeps, and a series of samples of the Columbia River up to 350 km downriver from the Hanford Site.

Spring vs. Fall RPH traverses • In both the fall and spring Richland traverses no detectable ^{236}U ($^{236}\text{U}/^{238}\text{U} < 2 \times 10^{-8}$) was found in the river to the east of an island that divides the flow. On the west side of the traverse the U contamination plume is outlined by $^{236}\text{U}/^{238}\text{U}$. The peak $^{236}\text{U}/^{238}\text{U}$ in the fall 2003 traverse was much higher than in the spring 2004 traverse. This suggests that the flux of contaminant U was less in the spring of 2004 compared to the fall of 2003. In fall 2003, the peak in $^{236}\text{U}/^{238}\text{U}$ occurred at about 100 m from the riverbank, while in spring 2004 the highest $^{236}\text{U}/^{238}\text{U}$ was measured in the nearest shore sample. This may be due to a change in the position of the contaminant source as is suggested by changes in contaminant source discussed below. Our U and Sr isotopic analyses of agricultural canals clearly demonstrate that they are the cause of relatively high U concentrations on the Franklin Co. side.

Locating sources and estimating U fluxes • In a plot of $^{238}\text{U}/^{235}\text{U}$ vs. $^{236}\text{U}/^{238}\text{U}$ the samples from the fall 2003 Richland and 300 Area traverses fall along a line extending from the composition of natural Uranium (Fig. 1). The U isotopic variation seen in those traverses can therefore be explained by mixing in various proportions between background natural U and a contaminant end-member that falls somewhere

further up that line. Comparison to data for 300 Area groundwater allows the identification of samples representative of the contaminant end members. For the fall 2003 traverse, a seep at the north end of the 300 Area is identified. In the case of the spring 2004 Richland traverse, a groundwater well (399-4-7) at the south end of the 300 Area is implicated to represent the contaminant U composition at that time. Based on these end-members, for the fall 2003 traverse the maximum percentage contaminant U in the fall 2003 Richland traverse was 34%, while for the spring 2004 traverse it was 20%. Based on the above, the observed plume geometry and estimated river flows we calculate the mass flux of contaminant U to the river. In fall 2003 on the order of 2 to 3 kg of contaminant U per day was introduced to the river (~4 % of the total natural U flux of the river), while in spring 2004 there was a flux of about 0.5 kg per day. The U contaminated groundwater volume was on the order of 20 to 30 kL/minute, but was less than half that in spring 2004. These fluxes must be considered approximate compared to our expected results from our fall 2004 traverse in which an ADCP was used to profile river flow velocity and directions. This will provide a highly determined context in which to derive contaminant U fluxes from our U isotopic data.

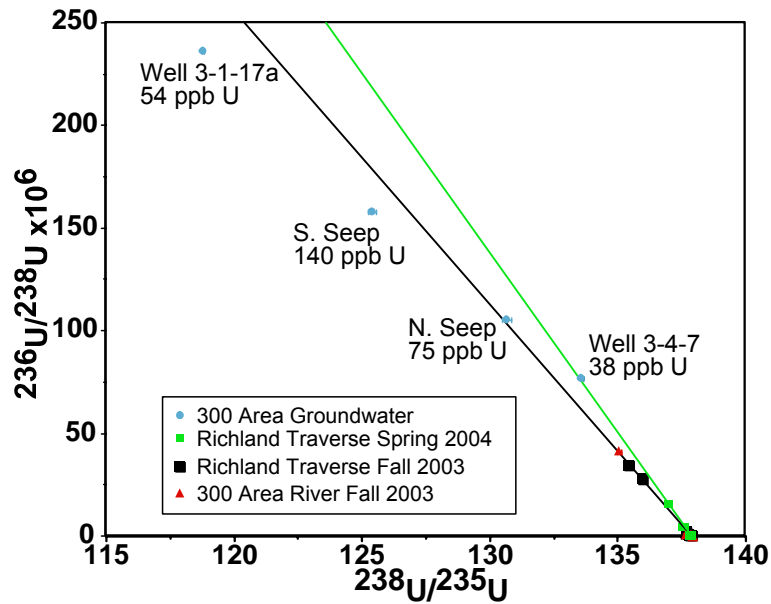


Figure 1. Plot of $^{238}\text{U}/^{235}\text{U}$ vs. $^{236}\text{U}/^{238}\text{U}$, showing Columbia River samples, and a set of samples (from wells and seeps) representing 300 Area groundwater.

Tracking the fate of Hanford U downriver • Our analyses of samples from the lower Columbia River demonstrate that ^{236}U can be detected at least 350 km downstream of the Hanford Site (Fig. 2). The U isotopic compositions of these samples are consistent with Hanford 300 Area groundwater U. Both U concentrations and $^{236}\text{U}/^{238}\text{U}$ decrease downstream (Fig. 2), indicating not only progressive dilution of the

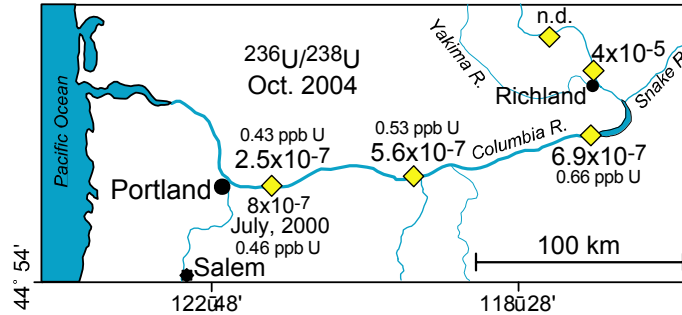


Figure 2. Map showing the decrease of $^{236}\text{U}/^{238}\text{U}$ downstream of the Hanford Site. No ^{236}U was detectable upstream of the Hanford, nor in the Yakima River. Also indicated are concentrations of U in ppb. Also shown is an archived sample collected in July 2000. All water samples were filtered to 0.45 microns.

Hanford U signature, but also suggests that U is being lost from solution. Further sampling, including the Snake River and other tributaries will help to resolve this. The $^{236}\text{U}/^{238}\text{U}$ for a 2000 sample is about 3 times higher than the corresponding 2004 sample, suggesting a decrease in the flux of Hanford U over that time. Further monitoring will determine whether this is a long-term trend. Our results so far clearly show the sensitivity of our technique in detecting and identifying contaminant U.

Identifying Sources of Groundwater Nitrate Contamination with Isotopic Measurements • Nitrate is a widespread groundwater contaminant at the Hanford Site. Possible sources for this contamination include high-level radioactive waste from leaking tanks or cribs, low-level waste derived from site activities, and leaching from soils and caliche layers in the vadose zone. Using a microbiologically-based technique for analyzing the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of dissolved nitrate, we have been able to determine unique isotopic signatures that can be used to distinguish the waste from normal background sources of nitrate (Singleton et al., 2005). Nitrate associated with high-level waste is characterized with high $\delta^{15}\text{N}$ (>10‰) and normal $\delta^{18}\text{O}$ (~5‰). Low-level waste nitrate has high $\delta^{18}\text{O}$ (>10‰) with low normal $\delta^{15}\text{N}$ (<5‰). This is particularly valuable for identifying potential high-level waste plumes as nitrate is a relatively conservative tracer of water movement in the vadose zone and groundwater and can be used to recognize possible problem areas where no radioactive contamination may yet be present.

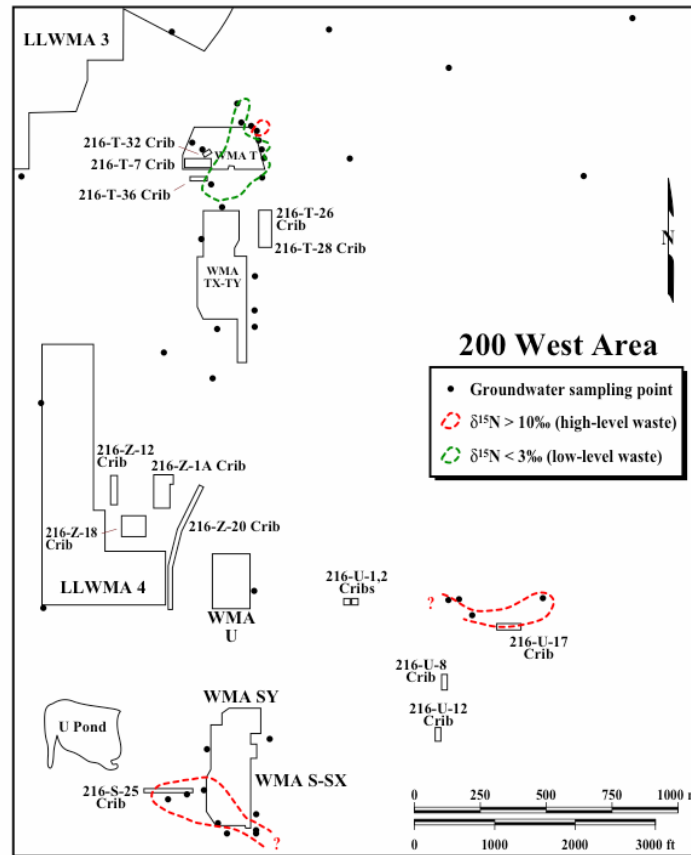


Figure 3. Map of the 200 West Area at Hanford showing the locations of groundwater samples for which the isotopic composition of nitrate has been analyzed with areas of high $\delta^{15}\text{N}$ ($>10\text{‰}$) and low $\delta^{15}\text{N}$ ($<3\text{‰}$) outlined. The high $\delta^{15}\text{N}$ nitrates are characteristic of nitrate associated with high-level radioactive waste. The nitrate in the low $\delta^{15}\text{N}$ zone centered on the WMA T area also has high $\delta^{18}\text{O}$ values ($>10\text{‰}$) characteristic of low-level waste. Nitrate concentrations in this area are highly elevated (to >3000 ppm).

The isotopic compositions of nitrate in approximately 150 groundwater samples from the Hanford Site have been measured. Several potential plumes of high-level waste nitrate have been identified with these data, including three sites in the 200 West Area (see Fig. 3). One of the high-level waste sites in the 200 West Area, the WMA T area, is the focus of an on-going investigation to identify the source of elevated ^{99}Tc in the groundwater. At this site, there appears to be two separate sources of nitrate contamination, one source associated with the ^{99}Tc that has a high-level radioactive waste signal and one source derived from very high concentration, low-level nitrate waste discharged to the vadose zone in the vicinity of WMA T. The other two areas of high-level waste nitrate, the 216-U cribs and the WMA S-SX area (Fig. 3) are associated with elevated uranium concentrations in the groundwater derived from high-level waste. By combining the nitrate isotope measurements with uranium isotope measurements, we hope to be able to pinpoint specific sources of high-level waste in groundwater at Hanford.

PLANNED ACTIVITIES

1. Integration of ADCP data with completed U isotopic data for fall 2004 traverses. This will provide a much more accurate and precise measure of the contaminant U flux to the river.
2. Li, B and Cr isotopic analyses of groundwater and porewater samples. Boron isotopic composition

can be an indicator past and present water pH and may be valuable means for tracing contaminated fluids and their interaction with sediments. Chromium isotopic analyses are being developed to trace Cr contamination and, because Cr isotopes can be fractionated during reduction, to monitor remediation efforts of Cr reduction.

3. U isotopic mapping of the 300 Area (as part of general groundwater mapping). This will provide constraints on the history of groundwater contamination in the 300 Area, as well as on the dynamics of the interaction between the Columbia River and 300 Area groundwater.

INFORMATION ACCESS

PEER-REVIEWED ARTICLES PUBLISHED IN OR SUBMITTED TO SCIENTIFIC JOURNALS

1. Singleton, M.J., Woods, K.N., Conrad, M.E., DePaolo, D.J., and Dresel, P.E. (2005) Tracking sources of unsaturated zone and groundwater nitrate contamination using nitrogen and oxygen stable isotopes at the Hanford Site, WA: *Environ. Sci. Technol.* 39, 3563-3570.
2. Singleton, M.J., Maher, K., DePaolo, D.J., Conrad, M.E., and Dresel, P.E. (in press) Dissolution rates and vadose zone drainage from strontium isotope measurements of groundwater in the Pasco Basin, WA unconfined aquifer: *J. Hydrology*.

PRESENTATIONS AT SCIENTIFIC MEETINGS

1. Singleton, M.J., Conrad, M., Woods, K., DePaolo, D., and Dresel, P.E. (2004) Connecting vadose zone nitrate to groundwater contamination at the Hanford Site with stable isotopes: *Geol. Soc. Am. Ann. Meeting and Exp., Denver, CO., Paper No. 137-5*.
2. Christensen, J.N., Dresel, P.E., Conrad, M.E., Patton, G.W., and DePaolo, D.J. (2004) Tracing and apportioning sources of uranium to the Hanford Reach of the Columbia River using uranium isotopes: *AGU 2004 Fall Meeting. Eos, Transactions, American Geophysical Union, 85(47): p. F858*.