Isotopic Tracers for Biogeochemical Processes and Contaminant Transport: Hanford, Washington

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Introduction

Our goal is to use isotopic measurements to understand how contaminants are introduced to and stored in the vadose zone, and what processes control migration from the vadose zone to groundwater and then to surface water. We have been using the Hanford Site in south-central Washington as our field laboratory, and our investigations are often stimulated by observations made as part of the groundwater monitoring program and vadose zone characterization activities. Understanding the transport of contaminants at Hanford is difficult due to the presence of multiple potential sources within small areas, the long history of activities, the range of disposal methods, and the continuing evolution of the hydrological system. Observations often do not conform to simple models, and cannot be adequately understood with standard characterization approaches, even though the characterization activities are quite extensive. One of our objectives is to test the value of adding isotopic techniques to the characterization program, which has the immediate potential benefit of addressing specific remediation issues, but more importantly, it allows us to study fundamental processes at the scale and in the medium where they need to be understood. Here we focus on two recent studies at the waste management area (WMA) T-TX-TY, which relate to the sources and transport histories of vadose zone and groundwater contamination and contaminant fluid - sediment interaction.

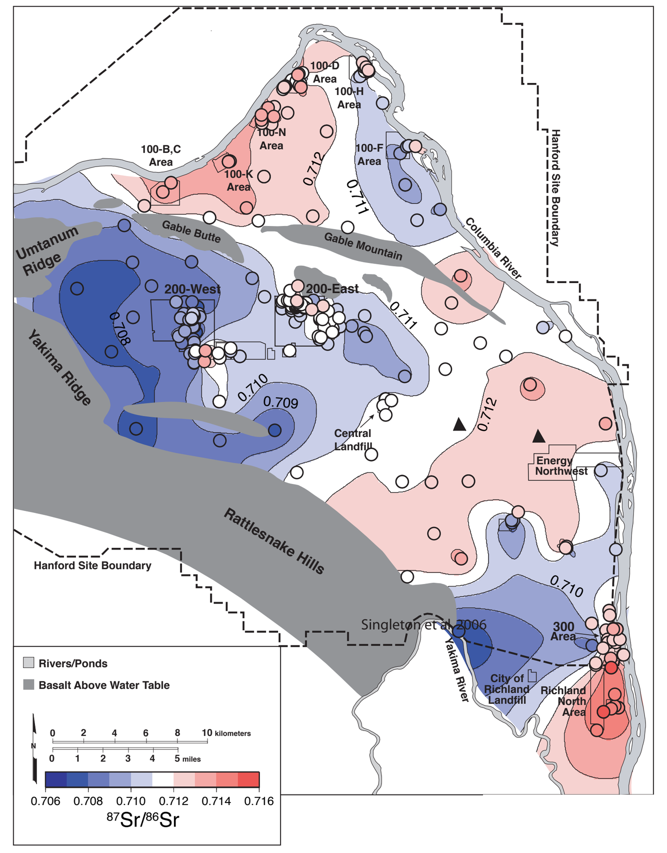

Figure 1. Groundwater Sr isotopic map for Hanford

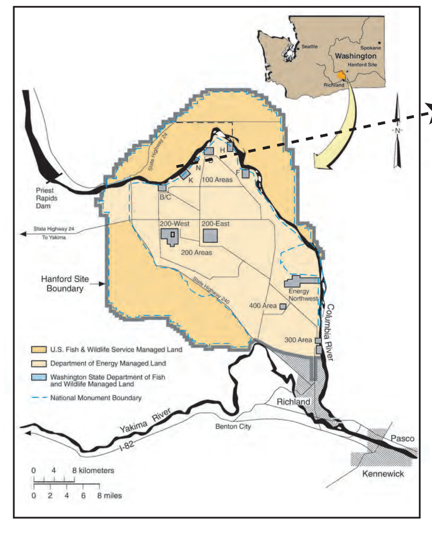

Figure 2. The Hanford Site

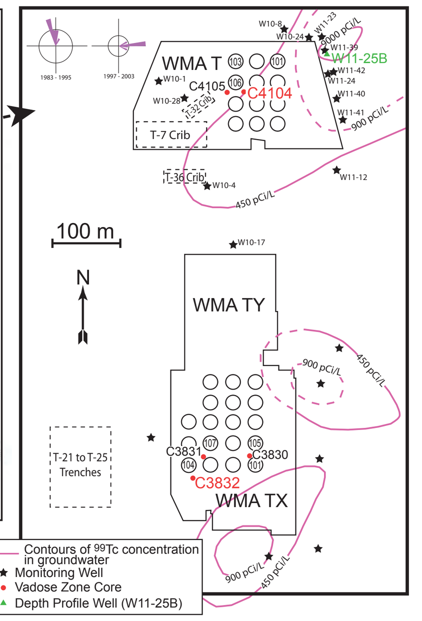

Figure 3. Map of the WMA T-TX-TY. Rose diagrams show groundwater flow directions for 1983-95 and 1997-2003 (Horton 2007).

The WMA-T and WMA-TX-TY tank farms are located within the 200 West Area in the central portion of the Hanford Site (Fig. 2). They present a complicated picture of mixed groundwater plumes of nitrate, ^{99}Tc, Cr^{6+}, carbon tetrachloride, etc. and multiple potential vadose zone sources such as tank leaks and disposal cribs (Fig. 3). To access potential vadose zone sources, we analyzed samples from cores C3832 near tank TX-104 and from C4104 near tank T-106. Tank T-106 was involved in a major event in 1973 in which 435,000 L of high activity waste leaked to the vadose zone over a seven-week period. Other nearby tanks (T-103 and T-101) are also suspected of having leaked or overfilled. Pore water from these cores was analyzed for U and Sr isotopic compositions.

Increasing ^{99}Tc concentration in monitoring well 299-W11-39 (to 27,000 pCi/L in 2005) near the northeast corner of the WMA-T area prompted the emplacement of a series of new wells, 299-W11-25B, W11-45 (down gradient), and W11-47 (Fig. 3), during which depth discrete samples were collected below the groundwater surface. The depth profile from W11-25B revealed high ^{99}Tc concentrations peaking at 182,000 pCi/L at ~10 m below the water table (Dresel et al. 2006). We obtained aliquots for isotopic analysis of groundwater samples produced by purge-and-pump sampling during the drilling of W11-25B, -45 and -47. In addition we have analyzed groundwater samples from monitoring wells in the vicinity of WMA T-TX-TY.

U Isotopes Track Contamination to its Source and Provide Clues to Chemical Interaction with Sediment.

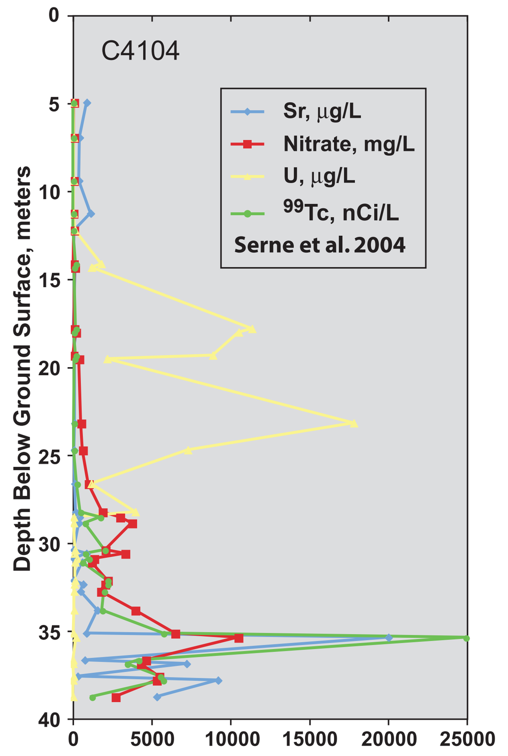

Figure 4.

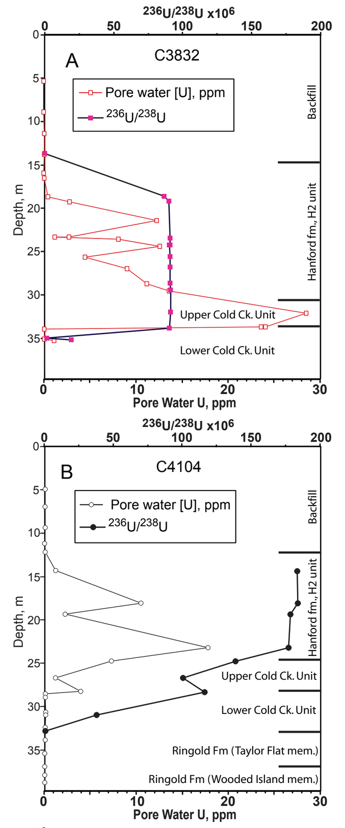

Figure 5.

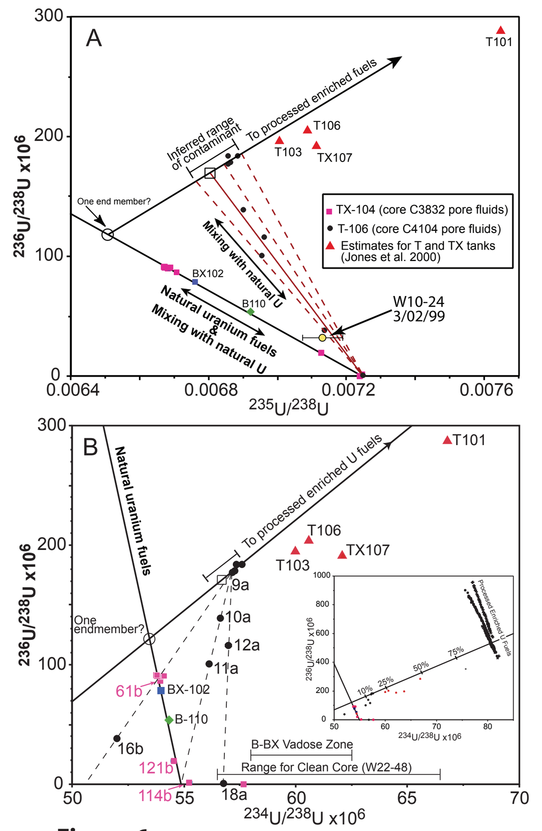

Figure 6.

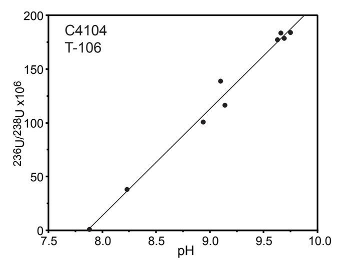

Figure 7. $^{236}U/^{238}U$ vs. pH for porewaters from core C4104 near tank T-106.

- ★The U in core C3832 is from processed natural U fuel, and is consistent with a suspected leak near tank TX-104 (Fig. 6A).
- ★The U in core C4104 represents a mixture of processed natural and enriched U fuels (the latter component varying down hole from 16% to 9%) (Fig. 6A and 6B).
- ★The isotopic compositions of the U components in C4104 are consistent with the 1973 T-106 leak event.
- ★The inferred $^{234}U/^{238}U$ of the background natural U component in some samples points to chemical interaction between contaminant fluid (high pH) and sediment (Fig. 6B).

Sr Isotopes of Porewater: Further Evidence of Reaction

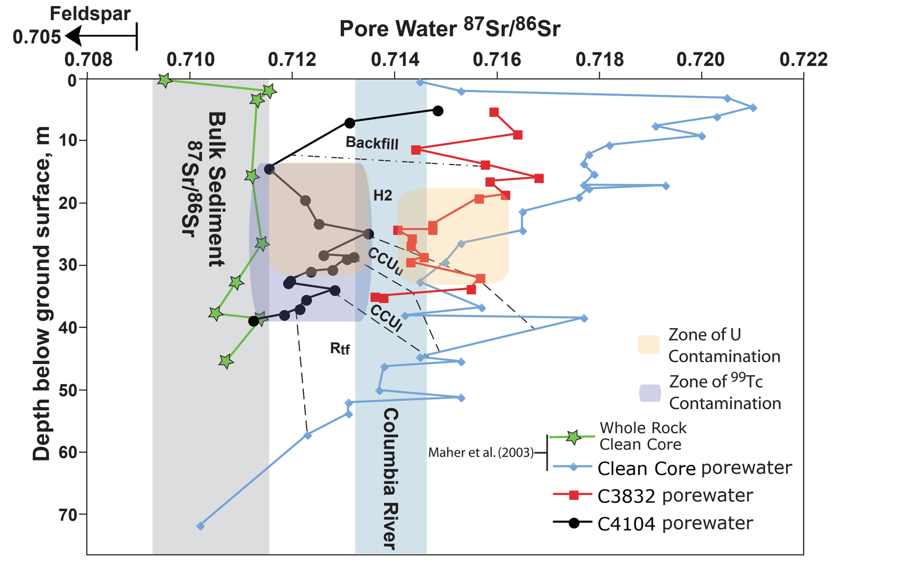

Figure 8.

★The Sr isotopic profiles of C4104 and C3832 are both shifted away from the profile of a nearby clean core toward the range of bulk sediment. This suggests release of low $^{87}Sr/^{86}Sr$ from the whole rock (or feldspars) due to chemical interaction between the contaminant fluid and the sediment.

Sr isotopes and vadose zone infiltration: Our previous studies show that groundwater under the 200 Areas at Hanford has background values of $^{87}Sr/^{86}Sr$ of 0.708 to 0.710 (Fig. 1), whereas labile Sr in the vadose zone has higher $^{87}Sr/^{86}Sr$ of 0.714 to 0.720. When large amounts of water are flushed through the VZ, the vadose zone Sr is carried down to the water table, causing an increase in the groundwater $^{87}Sr/^{86}Sr$, and producing a vertical gradient in $^{87}Sr/^{86}Sr$ below the water table.

Sr isotopes and sediment dissolution: The Sr-bearing minerals in the Hanford vadose zone contain Sr with $^{87}Sr/^{86}Sr$ that is lower than that in the labile fraction of the VZ. Hence if Sr is released by mineral dissolution, the $^{87}Sr/^{86}Sr$ of the dissolved Sr in pore fluid tends to decrease.

Sr Isotopic Map and Profiles of Groundwater: Tracking Mixing and Sources of Contamination

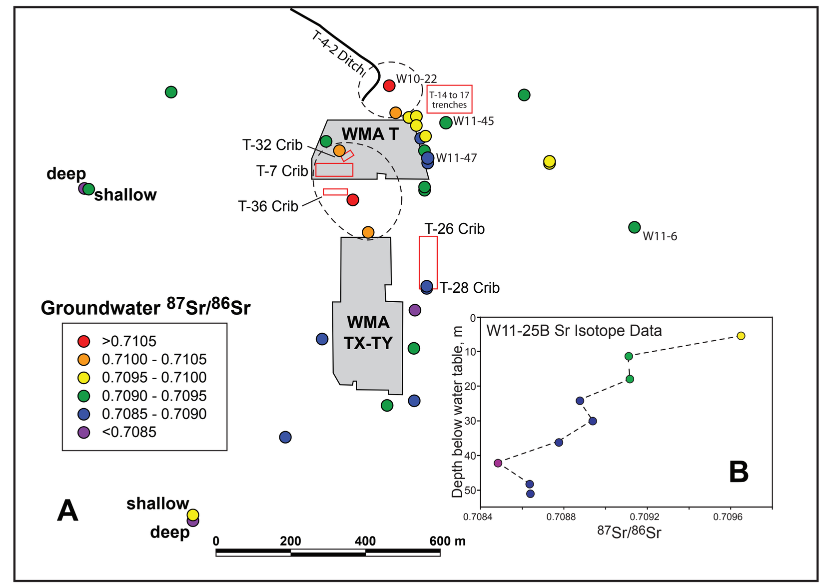

Figure 9.

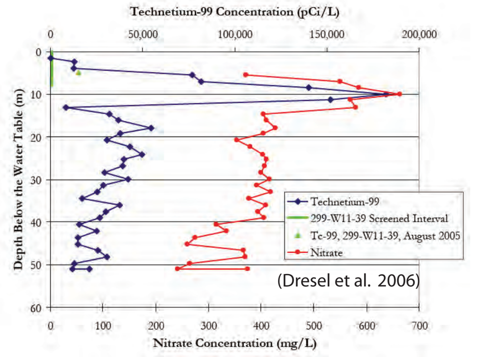

Figure 10. Vertical distribution of ^{99}Tc and nitrate in W11-25B.

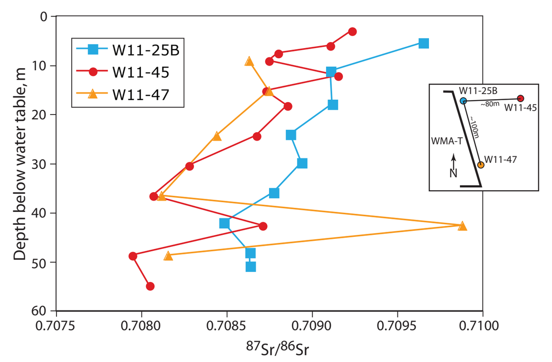

Figure 11. Vertical profiles of $^{87}Sr/^{86}Sr$ for wells W11-25B, W11-47 and W11-45, which is 80m downgradient of W11-25B (see inset).

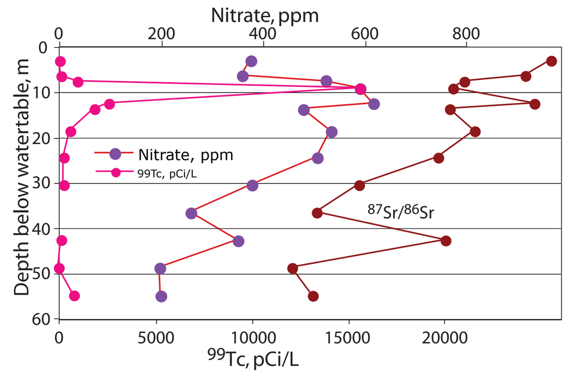

Figure 12. Vertical profiles of ^{99}Tc and nitrate concentrations in W11-45 compared to the $^{87}Sr/^{86}Sr$ profile (shown without scale).

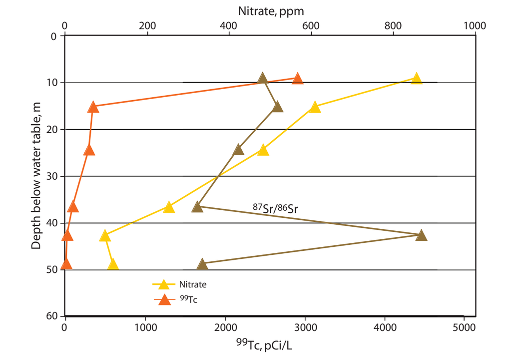

Figure 13. Vertical profiles of ^{99}Tc and nitrate concentrations in W11-47 compared to the $^{87}Sr/^{86}Sr$ profile (shown without scale).

★Groundwater map of $^{87}Sr/^{86}Sr$ for the WMA T-TX-TY identify areas of enhanced recharge through the vadose zone (Fig. 9):

1. Cribs in the WMA-T
2. North of WMA-T near the 216-T-4-2 ditch
3. The NE corner of WMA-T

★Vertical profiles of $^{87}Sr/^{86}Sr$:

1. Reflect input and mixing of high $^{87}Sr/^{86}Sr$ from the vadose zone (Fig. 11)
2. Provide evidence of multiple levels of preferred horizontal transport (Figs. 11 and 12)
3. Indicate separate sources for the peak ^{99}Tc concentration and the deeper nitrate peak (Fig. 12)

$\delta^{15}N$ and $\delta^{18}O$ of Nitrate: Tracing its Sources and its Co-Contaminants

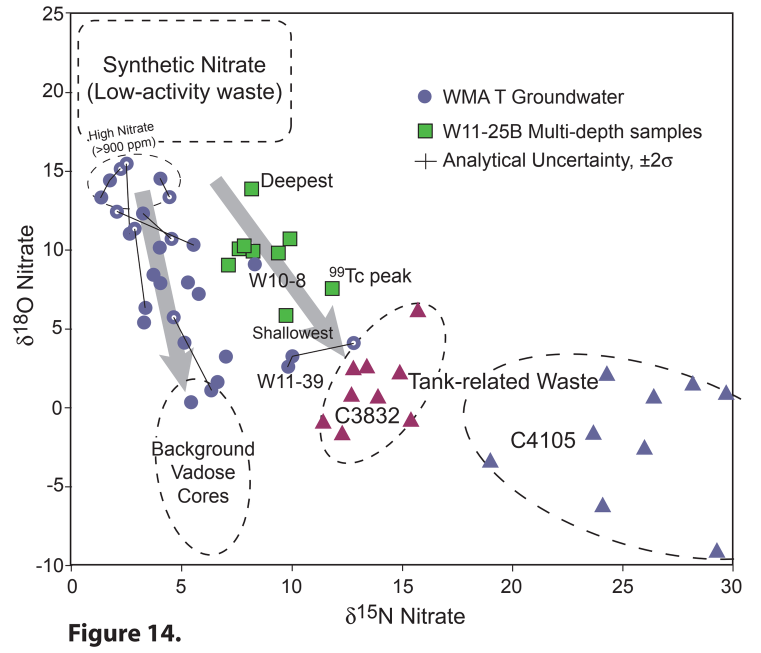

Figure 14.

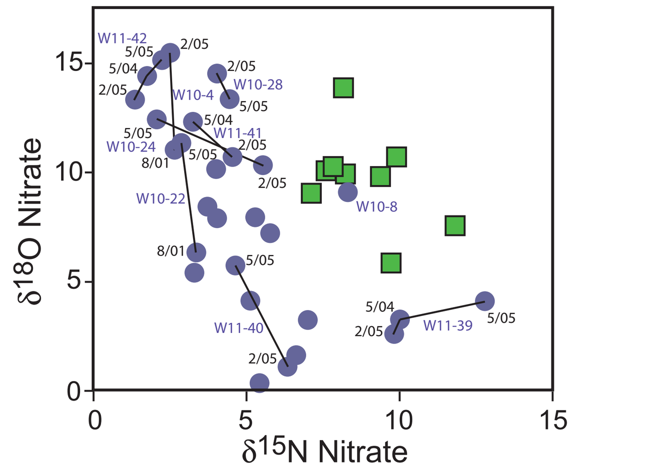

Figure 15. Detail of Fig. 14 illustrating changes in nitrate isotopic composition with time. Lines connect samples from the same well, numbers are sampling dates.

★The high ^{99}Tc observed in the NE corner of the WMA-T is likely associated with nitrate derived from tank-related waste, possibly from the 1973 T-106 spill (Fig. 14).

★The broader nitrate plume in the WMA-T represents a mixture of nitrate from low-activity waste and background nitrate flushed from the vadose zone (Fig. 14).

★A likely source for the WMA-T nitrate plume are the T-7 and T-32 cribs (Fig. 3)

Future Work

1. U isotopic study of the dynamics of the 300 Area U contamination plume, isotopic analysis of 300 Area sediments, including column experiments.

2. Cr isotopic study of remediation efforts (in situ barrier and bio-stimulation) of Cr^{6+} plume in the 100D Area.

3. Investigation of isotopic signatures of sulfate ($\delta^{34}S$ and $\delta^{18}O$) to trace sources of co-contaminants, and as a probe of redox processes affecting the mobility of redox sensitive metals like Cr.

Conclusions

1. U and Sr isotopic analyses of vadose zone porewater can provide evidence of chemical interaction between sediment and contaminant fluids.

2. Combining isotopic signatures of multiple components provides a powerful means to trace the source and fate of contaminates.

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