

# **Field Evidence for Strong Chemical Separation of Contaminants in the Hanford Vadose Zone**

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## **ABSTRACT**

Water and chemical transport from a point source within vadose zone sediments at Hanford were examined with a leak test consisting of five 3800-liter aliquots of water released at 4.5 m depth every week over a 4-week period. The third aliquot contained bromide, D<sub>2</sub>O and <sup>87</sup>Sr. Movement of the tracers was monitored for 9 months by measuring pore water compositions of samples from boreholes drilled 2-8 m from the injection point. Graded sedimentary layers acting as natural capillary barriers caused significant lateral spreading of the leak water. D<sub>2</sub>O concentrations >50% of the concentration in the tracer aliquot were detected at 9-11 m depth. However, increased water contents, lower  $\delta^{18}\text{O}$  values, and geophysical monitoring of moisture changes at other depths signified high concentrations of leak fluids were added where D<sub>2</sub>O concentrations were <3% above background, suggesting limited mixing between different aliquots of the leak fluids. Initially high bromide concentrations decreased more rapidly over time than D<sub>2</sub>O, suggesting enhanced transport of bromide due to anion exclusion. No significant increase in <sup>87</sup>Sr was detected in the sampled pore water, indicating strong retardation of Sr by the sediments. These results highlight some of the processes strongly affecting chemical transport in

the vadose zone and demonstrate the significant separation of contaminant plumes that can occur.

## INTRODUCTION

Fluid flow and chemical transport in unsaturated sediments are complex processes that are highly dependent on a wide range of factors. Seasonal variations in temperature, the volume and nature of precipitation determine the amount of water available for infiltration. In near-surface layers, evaporation and plant transpiration strongly affect whether the water is recycled to the atmosphere or migrates into the deeper subsurface. Once the water has passed through the root zone, relatively minor variations in the grain-size of the matrix can lead to significant lateral transport of the fluids (Stephens and Heerman, 1988; Kung, 1990a; 1990b). Locally, infiltration along high-permeability fracture zones can greatly accelerate water transport (Scanlon et al., 1997). For chemical transport, processes such as sorption, anion exclusion and colloidal transport further complicate the picture (Gvirtzman and Gorelick, 1991; Brusseau, 1994).

Where the fluid source is localized in time and/or space, such as an accidental spill or leak from a holding tank or pipe, transient flow fields may occur that differ significantly from normal background conditions. This is of special concern when the leak fluids contain chemical contamination that poses a potential threat to groundwater resources. Tracking fluid and chemical movement under these conditions is a complicated issue that generally requires the use of several complementary monitoring techniques to fully understand what is happening. Geophysical techniques including neutron moderation, electrical resistance and crosswell radar tomography can accurately detect changes in moisture content in the vadose zone (e.g., Hubbard et al., 1997; Binley et al., 2002; Alumbaugh et al., 2003). Tracers can be used to examine transport of chemicals, but processes such as sorption and retardation may make it unclear how

they interact with the matrix under unsaturated conditions. Natural variations in the stable hydrogen ( $\text{D}$ ) and oxygen ( $^{18}\text{O}$ ) isotopic compositions of water can also be used to track water in the vadose zone. These isotope tracers are water with the same properties as those of natural water and are not affected by the chemical and physical processes that affect other tracers making them ideal tracers for water. Where natural differences in the isotopic compositions of the different fluids are not significant, it is possible to use water labeled with  $\text{D}_2\text{O}$  and/or  $\text{H}_2^{18}\text{O}$  (Swenson, 1997; Anderson et al., 1997).

In this paper, we present data from a field experiment at the Hanford Site designed to simulate the movement of water and chemicals released from a point source (e.g., a leaking tank). The primary purpose of this test was to identify the principal mechanisms controlling vadose zone transport processes at the site (Ward and Gee, 2000).  $\text{D}_2\text{O}$  was added to the third of five aliquots of water released into the subsurface in order to track the migration of the water and examine its interaction with the other four aliquots of leak water and the ambient pore water. In addition to  $\text{D}_2\text{O}$ , the tracer aliquot also contained bromide and other stable isotopic tracers (e.g.,  $^{87}\text{Sr}$ ) to examine how chemical transport in the vadose zone is affected by interaction with the sediments.

## **MATERIALS AND METHODS**

### **Site Background**

The Hanford Site is located in the Pasco Basin in south-central Washington, about 10 km north of the confluence of the Columbia and Yakima rivers (Figure 1). Between 1944 and 1986, the site was used for production and refining of plutonium for nuclear weapons. During this time, chemical separation and refining of the plutonium was done in the 200 Areas. Radioactive

waste generated from these activities is stored in buried tanks in the 200 Areas, many of which are known to have leaked in the past (late 1950s to late 1970s) when they contained large volumes of drainable liquids. At the present time, most of the drainable liquids have been removed and no further leaking has been observed. In addition to the tank fluids, large quantities of low-level waste were discharged directly to the ground through infiltration ponds, open trenches, and cribs (buried, open-bottomed containers). As a result of these practices, there is considerable radionuclide contamination in the vadose zone beneath the 200 Areas. Some of this contamination has reached the groundwater and low levels have been detected in the Columbia River. Understanding the pathways and mechanisms of movement of the waste fluids in the vadose zone is critical for assessing the potential threat to human health and the environment posed by these contaminants.

The general geology of the Hanford site consists of sedimentary deposits overlying tholeiitic basalt flows of the Columbia River Basalt Group (Reidel et al., 1994; Slate, 1996; Reidel, 1998). The uppermost sedimentary formation in the 200 Area plateau is the Hanford Formation. The thickness of the Hanford Formation in this area is up to 100 m. It was deposited by cataclysmic flood events during Pleistocene glacial periods. The floods occurred when ice dams forming massive glacial lakes (e.g., Lake Missoula in northern Idaho/Montana) were breached. The age of the Hanford Formation was believed to be restricted to the late Wisconsin (12 to 16 Ka), but recent Th/U age determinations and paleomagnetic data suggest that it was deposited during glacial periods throughout the Pleistocene (Bjornstad et al., 2001).

During flood events, the water would collect in the Pasco basin and slowly drain out through the Wallula Gap (Allison, 1933). This led to three basic types of sedimentary deposits: (1) Gravel-rich units formed in high-energy channels; (2) Thick sequences of coarse- to fine-grained

sands were deposited adjacent to the main channels; (3) Rhythmic graded beds consisting primarily of silt with minor sand and ranging from 0.1 to 1 m thick were formed in slack-water areas (Baker et al., 1991). These different units have significantly different hydrologic properties that strongly influence the transport of contaminants, especially in the vadose zone.

In May and June of 2000, a mock tank leak test was carried out at the 299-E24-111 Experimental Test Well Site (also known as the Sisson and Lu site) in the 200 East Area (Figure 1). This time period was chosen because precipitation in the area is generally minimal during the late spring and summer (no measurable precipitation occurred during the test), so natural infiltration was not a factor. The Sisson and Lu site was the location of a series of earlier tracer tests using nitrate, chloride, barium, rubidium, calcium and the short-lived radionuclides  $^{134}\text{Cs}$  and  $^{85}\text{Sr}$  conducted during the early 1980s (Sisson and Lu, 1984). Figure 2 is a schematic map of the site showing the locations of a set of steel-cased wells that were installed for those earlier studies. Also shown on Figure 2 are the locations of the injection well, the sampling boreholes drilled after the injection test, and wells installed for cross-well radar and seismic studies for this test.

For this test, 5 aliquots of ~3800 liters (1000 gallons) each of water were leaked into the subsurface at the Sisson and Lu site at weekly intervals, following the general protocol used for the earlier sets of tracers studies done at the site during the 1980s (Sisson and Lu, 1984). The water was gravity-fed into the sediments at a depth of 4.5 m through a 15 cm inner diameter cased borehole (taking approximately 8 hours to infiltrate into the sediments). The third aliquot of water contained 2 kg of  $\text{D}_2\text{O}$ , 3 g  $\text{NaH}^{13}\text{CO}_3$ , 25 mg  $^{87}\text{Sr}$ , 1 mg  $^{145}\text{Nd}$ , 1 mg  $^{179}\text{Hf}$ , 3 mg  $^{207}\text{Pb}$  and 1000 ppm of bromide. Transport of the tracers with time was monitored by analyzing the

isotopic compositions of the tracers and the bromide concentrations in pore water extracted from core samples from the S boreholes.

The geology of the Sisson and Lu site consists of coarse- to fine-grained sands and silts from the upper part of the Hanford Formation. Last and Caldwell (2001) and Last et al. (2001) identified six distinctive units in the upper 17 m of the sediments (the sequence where the tracer tests were conducted) that could be correlated between boreholes. The stratigraphic column in Figure 3 summarizes this classification scheme. The key features of the sediments are the two strongly layered units at depths of 6-7 m (unit C) and 10-12 m (unit E).

Also plotted on Figure 3 are the moisture contents of the sediments measured for samples from a borehole drilled before the leak test was conducted (Last and Caldwell, 2001). In the coarser, poorly laminated units, the water contents are generally low (~2 wt.% water). In the two layered units (C and E), the moisture contents of the sediments are higher (to >8 wt.% water), especially in the bottom meter of the lower layered unit. No measurements of the hydrogen and oxygen isotope ratios of the pore water in the pre-test borehole were done. However, the isotopic compositions of pore water samples from boreholes from several uncontaminated areas in the 200 Areas have been analyzed (DePaolo et al., 2004). In most cases, the oxygen isotopic compositions of the pore waters have been shifted to higher values relative to mean precipitation due to evaporation during infiltration. The magnitude of the isotopic shift varies, but is generally 2‰ to 4‰ for oxygen isotopes. The  $\delta^{18}\text{O}$  values of pore water from the Sisson and Lu site measured on core samples that were not affected by the leak fluids were similar to those from other vadose zone cores ( $\delta^{18}\text{O} = -14$  to  $-16$ ), suggesting that the background  $\delta^{18}\text{O}$  values at the site were probably in the same range as other vadose zone pore waters at Hanford.

## Core Sampling

The S-2 and S-3 cores were drilled with a 25 cm (10 in) outer diameter hollow stem auger. Core samples were collected by removing the bit on the auger and driving a 7.6 cm (3 in) inner diameter, 0.6 m (2 ft) long split spoon sampler into the undisturbed sediments beneath the auger. The split spoon sampler included four 15 cm (6 in) Lexan® liners. After the sampler was retrieved, the Lexan® liners were removed from the sampler and capped at both ends. The auger bit was replaced and advanced to the next interval to be sampled.

The later tracer cores (S-5, S-7 and S-8) were drilled using a cone penetrometer and a wireline sampling tool (Last et al., 2001). For each borehole, the cone penetrometer was initially pushed to 4.5 m depth. From that depth on, the cone was removed and replaced with the sampling unit (2.5 cm diameter and 30 cm in length). The cone penetrometer with the sampling unit was then pushed 30 cm at a time and retrieved. The sample was removed from the sampler and immediately placed in a sealed plastic bag, placed on ice and transported to the laboratory for sub-sampling.

The core samples were kept sealed and refrigerated until they could be sub-sampled. For the samples collected in Lexan sleeves, the sleeves and caps were cut longitudinally and the core split down the middle. To minimize evaporation, samples for measurements of the isotopic compositions of the pore waters were collected from the central part of the sampled interval immediately after the core was split open. For the samples collected with the cone penetrometer, the bags were opened and immediately sampled. From both sets of samples, approximately 200 g of material for isotopic analyses was placed into a wide-mouthed, plastic sample bottle and sealed.

## Analytical Methods

The pore water in the samples collected for isotope analyses was vacuum-distilled from the samples at 100°C at the Center for Isotope Geochemistry (CIG) at the E. O. Lawrence Berkeley National Laboratory (LBNL). Water contents were determined by weighing the samples before and after the water was extracted and dividing the difference by the weight of the dry sample. The water contents for the samples used for bromide analyses were determined at the Pacific Northwest National Laboratory (PNNL). For those samples, approximately 100 g of the wet sample was placed in a pan of known weight and dried in an oven at 105°C for 24 hour (Last and Caldwell, 2001; Last et al., 2001).

The water contents determined by the vacuum-distillation method were in very good agreement with those determined for the oven-dried samples. Where the water contents of splits of the same sample were measured by both methods, the results were generally within  $\pm 10\%$  of each other. Most of this variability is believed to be the result of the heterogeneity of the samples. The average water contents measured by both methods for samples from S-5 and S-7 (the two cores where splits of the same samples were analyzed) were within 0.1% of each other. This is critical for the isotope analyses, as it has been shown that yields of less than 98% of the total water in a sample can lead to significant shifts in the isotopic composition of the water (Araguás-Araguás et al., 1995).

The stable isotope compositions of the water samples were analyzed at the Center for Isotope Geochemistry (CIG) at LBNL. The hydrogen isotope ratios ( $\delta D$ ) of the waters were analyzed using the method of Venneman and O'Neil (1993). 3  $\mu$ l water samples were injected into evacuated Pyrex® tubes containing approximately 50 mg of zinc metal. The water was reduced to H<sub>2</sub> gas by baking the tubes for 20 minutes at 500°C.  $\delta D$  values of the H<sub>2</sub> gas were analyzed



using the VG Instruments Prism Series II isotope ratio mass spectrometer (Prism) at CIG. The oxygen isotope ratios ( $\delta^{18}\text{O}$ ) of the samples were analyzed using an Isoprep automated  $\text{CO}_2\text{-H}_2\text{O}$  equilibration system interfaced to the Prism. The isotope ratios are expressed as per mil deviations from an internationally accepted standard (V-SMOW). For hydrogen, duplicate analyses of the  $\delta\text{D}$  values of the waters were generally within  $\pm 2\%$ . For oxygen, the precision of the measurements is  $\pm 0.1\%$ .

Strontium isotope compositions ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) were measured for de-ionized water leaches of the dried sediment remaining after the pore water was removed by vacuum distillation method. 30 g of dried sediment were combined with 30 ml of 18M $\Omega$  de-ionized water, shaken for 90 minutes and allowed to stand for 24 hours. The strontium contained in the rinse water is assumed to be that which was originally dissolved in the pore fluid, plus any readily exchangeable strontium on the solid phases. The dissolved strontium was extracted from the rinse water using Eichrom Sr-Spec resin in 0.250 ml Teflon columns. Yields for the chemical separations were about 98%. Total procedural blanks were approximately 5 ng Sr, corresponding to  $<0.2\%$  of the total amount of Sr extracted. Given the small blank contribution relative to the total amount of Sr analyzed, no blank corrections were applied. Sr isotope ratios were measured on a VG354 multi-collector thermal ionization mass spectrometer in the CIG laboratories on the UC Berkeley campus. The average  $^{87}\text{Sr}/^{86}\text{Sr}$  value for NBS 987 during the analyses was  $0.710286 \pm 0.00002$  (2 $\sigma$ ).

## RESULTS

The water contents, hydrogen, oxygen and strontium isotope compositions of the pore waters extracted from the tracer cores are given in Table 1. Limited analyses were done for the other

isotopic tracers added to the leak fluids ( $\text{NaH}^{13}\text{CO}_3$ ,  $^{145}\text{Nd}$ ,  $^{179}\text{Hf}$ , and  $^{207}\text{Pb}$ ), but the results were inconclusive and are not discussed here.

The enrichment of the deuterium content of the pore water relative to the tracer solution ( $C/C_0$ ) is also given in Table 1. This was calculated by converting the measured  $\delta\text{D}$  values for the samples into D/H ratios using the following formula derived from the definition of delta values:

$$(\text{D}/\text{H})_{\text{sample}} = [(\delta\text{D})_{\text{sample}}/1000 + 1] \times (\text{D}/\text{H})_{\text{VSMOW}} \quad (1)$$

where  $(\text{D}/\text{H})_{\text{VSMOW}}$  is taken as 0.000156. The concentration of deuterium (in ppm) in the water was then determined from  $(\text{D}/\text{H})_{\text{sample}}$ . The  $C/C_0$  values for the samples were calculated using the following formula:

$$C/C_0 = [(\text{ppm D})_{\text{sample}} - (\text{ppm D})_{\text{background}}]/[(\text{ppm D})_{\text{tracer}} - (\text{ppm D})_{\text{background}}] \quad (2)$$

with a background concentration of 136.36 ppm D (corresponding to a  $\delta\text{D}$  value of -126‰; the average hydrogen isotope composition we have measured for pore water samples extracted from fine-grained units in the Hanford Formation) and a tracer concentration of 574.44 ppm D (from an average  $\delta\text{D}$  value of 2680‰ determined from measurements of 4 samples of the tracer solution). Given the uncertainties in the data collection and the initial isotopic compositions of the pore water and the tracer solution, the maximum error in the  $C/C_0$  values in Table 1 is estimated to be <0.01.

### **Boreholes S-2 and S-3**

Sampling boreholes S-2 and S-3 were both drilled approximately 2 m down gradient from the injection well, 21 and 25 days, respectively, after the tracer solution was leaked into the

subsurface (8 and 12 days after the final aliquot of water was released). The water contents,  $C/C_0$  for deuterium and bromide in the pore water, and the  $\delta^{18}\text{O}$  compositions of the pore water are all plotted versus depth on Figure 4. The bromide concentrations and the moisture contents for the bromide samples are from Last and Caldwell (2001). Also shown on Figure 4 are the approximate depths for the different units identified in Figure 3.

The highest water contents measured from both cores were in samples from the lower sections of units C and E, the two fine-grained units. However, these moisture contents are comparable to the water contents measured in S-1, the pre-injection core (Figure 3). The most significant increases in the water contents of the sediments were observed between 7 and 11 m depth (unit D and the upper part of unit E). The average water concentration in this interval more than doubled from 2.3 wt.% in S-1 to 5.1 wt.% in the S-2 and 5.5 wt. % in S-3. Above and below this interval, the water contents were essentially identical to those measured in S-1. These findings are similar to the results of neutron probe (Ward et al., 2000) and cross-well radar imaging (Majer et al., 2000) studies of the site conducted before and after the infiltration tests. Both of these studies clearly showed major increases in the moisture content of the sediments between 7 and 11 m with only minor increases in moisture beneath 12 m depth, even within Unit E, the lower, finer-grained, layered unit.

The  $C/C_0$  values measured for deuterium and bromide are plotted together in the central panels of Figure 4. High concentrations of both tracers were detected at 9 to 11 m depth in both cores, corresponding to the lower part of unit D and the upper part of unit E. There were also smaller peaks in the upper part of unit C (~6 m depth) in both cores. In addition, there was a single sample with a high concentration of deuterium ( $C/C_0 = 0.31$ ) at 13 m depth in borehole S-

2. There was a slight enrichment in bromide (~3%) in a sample collected just below this sample, but nothing nearly as high, suggesting that this represents an isolated fluid pathway.

The deuterium and bromide data clearly indicate that most of the tracer solution was spreading out laterally between the two layered units (units C and E). Peak tracer concentrations above the lower layered unit (E) reached greater than 50% of the initial concentration in the tracer solution, with  $C/C_0$  values for deuterium generally higher than for bromide. Given that the water content approximately doubled between the two layers, this implies that all of the added water at this depth was from the tracer aliquot. This is notable because the tracer solution represented only 20% of the total water released during the experiment. Furthermore, there were low concentrations of both tracers in the zone between 7 and 9 m depth where increased moisture contents were also observed.

The leak fluids also shifted the  $\delta^{18}\text{O}$  values of the pore waters. Although the  $\delta^{18}\text{O}$  values of the leak fluids were not intentionally altered, there was a large enough difference between the leak water (Columbia river water) and the pore waters (precipitation shifted by evaporation during infiltration) to detect the leak fluids. Based on the  $\delta^{18}\text{O}$  values of pore water samples from similar units in other cores and the  $\delta^{18}\text{O}$  values of the pore water from unaffected intervals of these cores (e.g., from unit B, the lower part of unit E and unit F), the background  $\delta^{18}\text{O}$  values of the pore water are estimated to be between -14.5 and -15.5‰, whereas the leak waters were approximately -17.5‰. Although this signal is not nearly as pronounced as the deuterium and bromide signals, it is significant enough to identify the presence of the leak fluids in the subsurface, and allows us to compare the distribution of the tracers, which were only added to the third leak aliquot, to the distribution of the total amount of leaked water.

The  $\delta^{18}\text{O}$  values of the pore water samples from both boreholes are plotted on right-hand side of Figure 4. Also shown is an outline of the deuterium data for the same samples. In general the results were similar, but there were some notable differences. Based on the  $\delta^{18}\text{O}$  data, all of the pore water between 7 and 11 m depth contained high proportions of the leak water (up to 70%), including areas that contained only minor enrichment of deuterium or bromide. This indicates that there was limited mixing between the different leak aliquots in the subsurface. The water from the tracer aliquot spread laterally mainly near the boundary between stratigraphic units D and E, whereas the water from all of the leaked aliquots is more evenly distributed within units C, D and E.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  values measured for pore water samples from S-2 and S-3 were between 0.7139 and 0.7153 (except for one sample from the bottom S-2 which had a value of 0.7118). One sample from Unit D in borehole S-1 had  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7140, which matches well with strontium isotope ratios reported by Maher et al. (2003) at similar depths in the Hanford Formation. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of the tracer solution was measured at 1.300. For Sr concentrations of 1.6 ppm in the pore water and 100 ppb in the tracer solution and a  $C/C_0$  of 0.5, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the pore water in the peak deuterium samples in S-2 and S-3 should be about 0.753 if strontium was acting conservatively. However, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in both cores were very close to background, indicating strong retardation of strontium in the sediments.

### **Borehole S-5**

A third borehole, S-5, was drilled at about 2 m from the injection hole on September 11, 2000 (88 days after the tracer solution was released). The data collected for S-5 are plotted on Figure 5. The average water content between 7 and 11 m depth in the core dropped to 4.1 wt.%

versus greater than 5 wt.% in the S-2 and S-3 cores, but was still significantly higher than before the test (based on changes in gravimetric water contents determined from bulk density estimates and volumetric water contents determined from neutron probe logging). This decrease is greater in the upper part of this zone (corresponding to the upper part of unit D) than in the lower part of the zone (corresponding to the lower part of unit D and the upper part of unit E).

The relative concentrations of deuterium and bromide in the S-5 pore water samples are plotted versus depth in the center part of Figure 5. The locations of the tracer peaks are similar to what was observed in boreholes S-2 and S-3. However, the concentrations of the tracers are lower. The peak deuterium concentration in S-5 is only 34% of the concentration in the tracer cocktail. Furthermore, the bromide concentrations in S-5 are significantly lower than the deuterium concentrations (less than half on average).

The  $\delta^{18}\text{O}$  data for the S-5 pore waters are plotted on the right-hand side of Figure 5. As with the S-2 and S-3 cores, the  $\delta^{18}\text{O}$  values of the pore water within the high water content zone at the base of unit D have been affected by the leak waters. In addition, the  $\delta^{18}\text{O}$  values of the pore water in the upper part of the core (above the 7 m high water content zone) are also shifted. There is one deep sample (at 16.6 m) with a shifted  $\delta^{18}\text{O}$  value and relatively high water content (4.5 wt. %). This sample suggests that water from some of the unlabeled leak aliquots may have penetrated to 16 m depth, but water from the tracer aliquot did not.

The strontium isotope ratios in the samples with elevated deuterium and bromide in this core are slightly enriched relative to the earlier samples (averaging 0.7154). This is much lower than would be expected ( $>0.73$ ) based on the level of deuterium enrichment, but could be an indication that there was limited transport of strontium during the infiltration experiments.

### **Boreholes S-7 and S-8**

The final two boreholes that were analyzed, S-7 and S-8, were drilled on 3/23/01, 281 days after injection of the tracer solution. S-7 was drilled about 3 m from the injection well and S-8 was drilled approximately 8 m from the injection well (Figure 2). The data from the S-7 samples are plotted on Figure 7 (including the bromide moisture contents and concentrations from Last et al., 2001). The water contents between 7 and 11 m depth average 3.4 wt. %, which is elevated relative to the pre-injection well (S-1), but significantly less than the concentrations in S-2, S-3 and S-5.

The bromide and deuterium concentrations in S-7 peaked at about the same depth as in the earlier boreholes (at the top of unit E, bottom of unit D). The relative concentration of deuterium in the highest sample ( $C/C_0 = 0.25$ ) had decreased relative to the peak concentration measured in S-5 ( $C/C_0 = 0.34$ ). The highest bromide concentration ( $C/C_0 = 0.08$ ) was found in the same sample, but it is less than a third of the deuterium concentration. The strontium isotope ratios of seven pore water samples from this core were also measured and were in the same range as background.

Pore water samples were extracted from only 3 samples from the S-8 core. However, the peak concentration of deuterium was at the same depth (11.4 m) as the peak bromide concentration (for which 20 samples were analyzed by Last et al., 2001).  $C/C_0$  for deuterium in that sample was 0.06, or ~25% of the peak concentration in S-7.  $C/C_0$  for bromide in the same sample was 0.08, higher than the value measured for deuterium. Furthermore, despite the greater distance from the injection point for S-8, the bromide concentration was essentially equal to the relative concentration measured in S-7.

## DISCUSSION

The results of the leak tests illustrate several important features of rapid infiltration of water coming from a point source within vadose zone sediments at Hanford (e.g., a tank leak). The geophysical monitoring of the infiltration tests very clearly demonstrated that most of the water released during the experiment spread out laterally between 4.5 m (the bottom of the injection well) and 11 m depth (Ward et al., 2000; Majer et al., 2000; Kowalski et al., 2005). Numerical simulations of the leak tests also predict significant lateral transport in the vadose zone (Ye et al., 2005; Ward et al., 2006). The tracer test data presented in this paper confirm this result and highlight several other important aspects of water movement and chemical transport in unsaturated, layered sediments.

### **Stratified Water Flow in the Unsaturated Zone**

The tracer data provide strong evidence that the different aliquots of leak fluids did not mix significantly as they moved laterally through the unsaturated sediments. In all four cores drilled at 2 to 3 m from the injection well (S-2, S-3, S-5, S-7), the moisture contents of the samples from between 6 and 11 m depth increased significantly relative to the moisture contents of the samples from the same interval in S-1, the pre-injection core, due to the addition of water from the leak aliquots. This is confirmed by both the geophysical data and the decrease in the  $\delta^{18}\text{O}$  values of the pore water samples. However, the zone of increased bromide and deuterium was more limited in extent, with the most highly enriched samples between 9 and 10 m depth. Furthermore, the peak  $C/C_0$  values for deuterium in S-2 and S-3 were 0.53 and 0.62, respectively. Given that the moisture content of these samples was approximately double the



pre-test concentrations in this interval, this indicates that most, if not all, of the added pore water at this depth was derived from the tracer aliquot and not the other four leak aliquots.

The average and peak  $C/C_0$  values for deuterium in all four of the boreholes are plotted versus the fraction of water added to the sediments on Figure 7. The fraction of “added water”,  $F_{\text{added water}}$ , was determined using the following formula:

$$F_{\text{added water}} = \frac{(\rho_{\text{peakD}} - \rho_{\text{initial}})}{\rho_{\text{peakD}}} \quad (5)$$

where  $\rho_{\text{peakD}}$  is the average moisture content in the interval containing the significantly elevated deuterium and bromide concentrations in each of the tracer cores and  $\rho_{\text{initial}}$  is the average moisture content between 9 and 11 m depth in S-1 (2.46%). The upper diagonal line across the figure has a slope of one and represents the position where a sample would plot if all of the added water in the sample were derived from the tracer aliquot. The lower line has a slope of 0.2 and is where the samples would plot if the added water contained 20% tracer solution (the fraction of the total leak water represented by the tracer aliquot). For all cases, at least 50% of the added water in this interval was derived from the tracer aliquot, especially in S-2 and S-3, the two cores drilled within two weeks after the final release of water. It is likely that the leak fluids displaced some of the pore water originally in the sediments, meaning that there is a greater fraction of added water. However, even if all of the original pore water was displaced, the tracer concentrations were still much higher than 20% in most cases. Conversely, if a similar analysis is done for samples with significant added water from above this interval, the  $C/C_0$  values for deuterium fall well below the slope 0.2 line. There was clearly limited mixing between the different aliquots of fluid released during the experiment, leading to strong vertical stratification of the fluids that persisted until 9 months after the leak test.

The implication of this result is that as the leak fluids filled the coarser-grained sedimentary layers, the unsaturated hydraulic conductivity of the layers would increase to the point where the fluid would begin to spread laterally. As different aliquots of the leak fluids were introduced, this occurred at different levels in the sediments, causing the waters from the different aliquots to spread along different layers in the sediments. This could result in different batches of waste fluids released from the same tank, infiltration pond or crib following different pathways through the unsaturated zone, eventually reaching the groundwater at different points.

### **Differential Transport of Deuterium and Bromide**

The observed movements of deuterium and bromide during this experiment were significantly different. In almost every case in the cores drilled within 2-3 m of the injection well,  $C/C_0$  for deuterium was higher than  $C/C_0$  for bromide. Furthermore, this relative difference increased with time. Figure 8 is a plot of the ratio of the relative concentrations of deuterium to bromide in the same zones of elevated tracer concentrations used for Figure 7. In S-2 and S-3, the average deuterium concentrations were approximately 1.5 times the average bromide concentrations. In S-5, that ratio of deuterium to bromide increased to greater than 2, and in S-7, drilled 9 months after the test, the ratio was greater than 3.5. Conversely, in S-8, which was drilled at the same time as S-7, but almost three times as far from the injection well, the ratio of deuterium to bromide was less than 1.

Even with the limited data, it is clear that the bromide is moving through the unsaturated sediments differently than the deuterium. Deuterium effectively represents the movement of the water and the peak bromide concentrations dissipated more rapidly than the peak deuterium concentrations. This implies that the spread of the bromide was limited to the faster flow paths

through the sediments. The most likely explanation for this is the process of anion exclusion (Gvirtzman and Gorelick, 1991). The negative charges on the surfaces of clay particles in the sediments repel the bromide anions in the tracer solution, preventing them from entering the narrower pore spaces that are accessible to the water. Since the bromide anions are restricted to the larger pore spaces where the fluid velocity is higher, the peak bromide concentrations will move through the sediments faster than the deuterium (although the initial breakthrough for both should remain the same).

If anion exclusion is an important process associated with chemical transport in the vadose zone, it could strongly effect of the appearance of different contaminants in the groundwater.  $^{99}\text{Tc}$  (as pertechnetate), nitrate and tritium are widespread contaminants and major components of many of the tank fluids. Anion exclusion could cause them to reach the groundwater sooner and/or in higher concentrations than some of the other less mobile contaminant species (e.g., uranium,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ), acting as a precursor to the arrival of high-level groundwater waste plumes.

### **Strontium Mobility**

There was limited evidence that the  $^{87}\text{Sr}$  in the tracer solution reached any of the boreholes sampled. The Sr concentration in the tracer solution was approximately 100 ppb with  $^{87}\text{Sr}/^{86}\text{Sr}$  of 1.3. For the other aliquots of leak water the concentration is also 100 ppb, but the  $^{87}\text{Sr}/^{86}\text{Sr}$  is about 0.714. The average pore water Sr concentration in vadose zone sediments of the Hanford formation is about 1600 ppb with  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.714 (Maher et al., 2003). With these numbers, we can calculate the expected  $^{87}\text{Sr}/^{86}\text{Sr}$  for the pore waters after the test for a range of  $K_d$  values. Those have been plotted on Figure 9 versus  $C/C_0$  for the tracer solution. Also plotted are the strontium isotope ratios for the pore water samples versus  $C/C_0$  for deuterium in the pore water

from the same sample. Given the uncertainties in the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of the background (pre-test) pore water (which probably ranged between 0.714 to 0.715), the lack of a discernible breakthrough for the  $^{87}\text{Sr}$  in the tracer aliquot is consistent with  $K_d$  values greater than 10. Column studies with Hanford sediments conducted by Um and Serne (2005) obtained  $K_d$  values for  $^{90}\text{Sr}$  of about 18 ml/g for coarse-grained Hanford sands.  $K_d$  values for finer sands from Hanford formation (such as those in this study area) are estimated to be 40 to 50 ml/g (R.J. Serne, personal communication).

## CONCLUSIONS

The results of the infiltration test demonstrate some of the complexity of chemical transport in the Hanford vadose zone. The layering in the sediments at the test site caused extensive lateral transport of leak fluids. This was further complicated by vertical stratification of flow with time, segregating the different leak aliquots at different levels within the active flow horizon. Chemical transport at the site was also strongly affected by interaction with the sediments. Anion exclusion led to accelerated transport of bromide relative to the bulk fluid (represented by deuterium). Conversely, sorption and exchange of dissolved strontium with the sediments strongly retarded its transport.

The implications of these results for contaminant transport at Hanford are significant. It is possible that contaminated water from a point source (e.g., leaking tank, crib) could travel substantial horizontal distances before infiltrating deeper into the sediments. How far is not clear (certainly on the order of tens of meters) and will depend on the types of sediments and the amount and continuity of any layering. In addition, the chemical composition of the waste fluids could be greatly altered by interaction with the sediments, separating the different chemical

components from each other. This makes it difficult to predict when and if the different contaminants will reach the groundwater.

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## Figure captions

**Figure 1.** Map of the Hanford site showing the location of the E24-111 Experimental Test Well (“Sisson and Lu”) Site.

**Figure 2.** Map of the Sisson and Lu Site showing the position of the injection well and monitoring wells used for the infiltration tests discussed in this paper.

**Figure 3.** Stratigraphic column for the Sisson and Lu site and moisture contents measured for samples from the S-1 (pre-injection test) core (Last and Caldwell, 2001).

**Figure 4.** Plots of the moisture contents in the S-2 (drilled 21 days after tracer injection) and S-3 (drilled 25 days after tracer injection) cores, relative concentrations of bromide and deuterium, and the  $\delta^{18}\text{O}$  values of pore waters in the pore waters plotted versus depth. The dashed line on the  $\delta^{18}\text{O}$  plots represents the deuterium concentrations for comparison. The moisture content data and bromide concentrations are from (Last and Caldwell, 2001).

**Figure 5.** Plots of the moisture contents in the S-5 core (drilled 88 days after tracer injection), relative concentrations of bromide and deuterium, and the  $\delta^{18}\text{O}$  values of pore waters in the pore waters plotted versus depth. The dashed line on the  $\delta^{18}\text{O}$  plot represents the deuterium concentrations for comparison. The moisture content data and bromide concentrations are from (Last et al., 2001).

**Figure 6.** Plots of the moisture contents in the S-7 core (drilled 281 days after tracer injection), relative concentrations of bromide and deuterium, and the  $\delta^{18}\text{O}$  values of pore waters in the pore waters plotted versus depth. The dashed line on the  $\delta^{18}\text{O}$  plot represents the deuterium concentrations for comparison. The moisture content data and bromide concentrations are from (Last et al., 2001).

**Figure 7.** Average fraction of added water plotted against average and peak  $C/C_0$  for deuterium in core samples with elevated deuterium concentrations. Also plotted are 1:1 and 1:5 mixing lines.

**Figure 8.** Ratio of average relative concentrations of deuterium to bromide plotted versus time for samples with elevated tracer concentration from all 5 sampling wells.

**Figure 9.** Plot of strontium isotope ratios versus  $C/C_0$  deuterium for pore water samples. Also plotted are calculated strontium isotope ratios at varying strontium retardation factors.

**Table 1.** Isotope data for the VZTFS core samples.

Interval (ft)	Depth (m)	% Water	$\delta D$ (‰)	C/C <sub>0</sub> D	$\delta^{18}O$ (‰)	$^{87}Sr/^{86}Sr$
<b>S-2 Core</b>						
14.0-14.5	4.3	2.6	-123	0.00	-14.7	
18.5-19.0	5.7	4.0	323	0.16	-15.4	0.7147
22.5-23.0	6.9	6.2	-112	0.01	-15.8	0.7141
26.5-27.0	8.2	5.4	-28	0.04	-16.3	0.7153
30.5-31.0	9.4	7.0	513	0.23	-16.4	
32.5-33.0	10.0	4.8	1356	0.53	-16.3	0.7142
38.0-38.5	11.7	8.3	-112	0.01	-14.9	0.7139
43.0-43.5	13.2	4.3	749	0.31	-15.7	0.7153
48.5-49.0	14.9	3.3	-124	0.00	-15.2	
52.5-53.0	16.1	2.8	-119	0.00	-15.2	0.7118
<b>S-3 Core</b>						
15.5-16.0	4.8	2.0	-119	0.00	-14.8	
18.5-19.0	5.7	2.4	-123	0.00	-15.2	
21.5-22.0	6.6	5.0	-75	0.02	-16.4	0.7141
25.0-25.5	7.7	3.8	-85	0.02	-16.7	0.7144
29.5-30.0	9.1	4.8	1602	0.62	-16.5	0.7143
35.5-36.0	10.9	4.1	887	0.36	-16.5	0.7140
37.5-38.0	11.5	6.3	-30	0.03	-16.4	
39.5-40.0	12.1	6.4	-123	0.00	-14.8	0.7138
48.5-49.0	14.9	2.5	-122	0.00	-15.5	
52.0-52.5	15.9	2.4	-124	0.00	-15.2	0.7144
56.0-56.5	17.1	4.3	-125	0.00	-15.0	
<b>S-5 Core</b>						
19.0-20.0	5.9	4.8	-39	0.03	-16.4	0.7153
21.0-22.0	6.6	4.2	-123	0.00	-16.1	
23.0-24.0	7.2	7.6	267	0.14	-15.9	0.7158
28.0-29.0	8.7	3.4	679	0.29	-16.3	
30.0-31.0	9.3	4.5	817	0.34	-16.2	0.7154
34.0-35.0	10.5	5.3	105	0.08	-16.0	0.7150
37.0-38.0	11.4	7.5	-124	0.00	-15.0	0.7144
40.0-41.0	12.3	2.8	-129	0.00	-15.3	0.7148
43.0-44.0	13.3	2.8	-129	0.00	-14.9	
48.0-49.0	14.8	2.6	-131	0.00	-14.9	
51.0-52.0	15.7	3.5	-128	0.00	-15.3	
54.0-55.0	16.6	4.5	-125	0.00	-15.8	
57.0-58.0	17.5	2.8	-131	0.00	-14.6	

**Table 1.** Continued

Depth (ft)	Depth (m)	% Water	$\delta D$ (‰)	C/C <sub>0</sub> D	$\delta^{18}O$ (‰)	<sup>87</sup> Sr/ <sup>86</sup> Sr
<b>S-7 Core</b>						
19.0-20.0	5.9	4.2	-69	0.02	-17.0	0.7148
26.0-27.0	8.1	3.0	96	0.08	-17.7	0.7143
29.0-30.0	9.0	3.3	568	0.25	-17.1	0.7141
33.0-34.0	10.2	5.3	244	0.13	-16.3	0.7145
36.0-37.0	11.1	7.1	-101	0.01	-15.4	
37.0-38.0	11.4	6.0	-123	0.00	-15.3	0.7144
44.0-45.0	13.6	3.1	-132	0.00	-15.4	0.7142
49.0-50.0	15.1	3.6	-132	0.00	-15.3	0.7145
54.0-55.0	16.6	2.9	-134	0.00	-15.3	
<b>S-8 Core</b>						
20.0-21.0	6.2	4.3	-121	0.00	-13.9	
37.0-38.0	11.4	9.6	45	0.06	-14.6	
43.0-44.0	13.3	3.1	-106	0.01	-16.0	