Vadose Zone Transport Field Studies: Isotope Tracer Results

FY01 Annual Report

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Executive Summary

The isotopic compositions of samples from five additional cores drilled at the Sisson and Lu site have been analyzed during FY2001 to track the movement of isotopic tracers leaked into the subsurface during June of 2000. The results of this work indicate the following:

- At 3 to 4 m lateral distance from the injection well, deuterium and bromide from the tracer cocktail remained confined to a narrow portion of the unsaturated zone between two less-permeable layers.
- The bromide concentrations in the sediments drop off more rapidly over time than the deuterium concentrations.
- Shifts in the oxygen isotope ratio of the pore water suggest that the water leaked into the subsurface interacted with a larger fraction of the sedimentary column than indicated by the tracer solution alone.
- After 9 months, there was no clear evidence of the strontium in the tracer cocktail, indicating that it is strongly retarded by interaction with the sediments.
- The deuterium signal was still detected (although significantly attenuated) at the same depth in the sediments after injection of a dense, Na-thiosulfate solution during late March through May of 2001.

These data indicate that fluids leaked into the Hanford sediments have a strong tendency to spread out laterally rather than infiltrate straight down towards the water table. There is also strong evidence that the water (tracked by the deuterium) does not travel at the same rate as the dissolved constituents. The use of non-radioactive isotopic tracers as proxies for contaminants of concern at the site (e.g., deuterium for tritium, ^{87}Sr for ^{90}Sr) clearly represents a powerful tool for understanding the movement of the contaminants in the sediments.

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Introduction

The primary purpose of work done during FY2001 was to observe the movement of the isotopic tracers released at the Sisson and Lu site during FY2000. The original cocktail of non-radioactive isotopic tracers included 2 kg of D_2O, 3 g of $NaH^{13}CO_3$, 25 mg of ^{87}Sr, 1 mg of ^{145}Nd, 1 mg of ^{179}Hf, and 3 mg of ^{207}Pb added to 4000 L of water. This solution also contained 1000 ppm of bromide. The tracer solution was the third of five 4000-L aliquots of water leaked at 1-week intervals during June of 2000. To monitor the migration of these tracers through the subsurface, a series of cores was drilled at the site. During FY2000, samples from two of those cores (S-2 and S-3) were analyzed. These boreholes were drilled approximately 3 m from the injection well about 3 weeks after the tracer solution was leaked into the subsurface. During September of 2000, another borehole (WL-2) was drilled ~3 m from the injection well, but samples from that core were not analyzed until FY2001. In March of 2001 (~9 months after injection of the tracers), two additional boreholes were drilled and sampled for isotopic analyses just before another series of leak tests was performed with a dense, Na-thiosulfate solution. One of these boreholes (WL-3A) was drilled ~3.5 m from the injection well and the other (WL-4) was drilled ~8 m away. Samples from four additional boreholes (WL-7, WL-8, WL-9 and WL-10) drilled following the injection of Na-thiosulfate solutions were collected for isotopic analyses.

Prior Results

During FY2000, isotopic measurements were made on boreholes S-1 (a background hole drilled before the leak tests), S-2, and S-3. The stable isotope (δD and $\delta^{18}O$) and bromide concentrations were completed for S-2 and S-3. In addition, preliminary measurements were made of the $^{87}Sr/^{86}Sr$ and $^{145}Nd/^{144}Nd$ ratios of the pore water in all three cores. Table 1 contains updated information on the Sr, Nd, and Pb isotopic ratios of the pore water from these cores.

The deuterium and bromide data clearly indicated that most of the tracer solution was spreading laterally between two less-permeable layers located at approximately 7 and 12 m below the surface. Peak concentrations were ~60% of the initial composition of the tracer solution (C/C_o). This is significant, given that the tracer solution only represented 20% of the total water leaked at the site. Further, there was no evidence that the tracer solution mixed with a perched water body developed above the lower less-permeable layer. This was confirmed by oxygen isotope data and geophysical studies that indicated that essentially none of the water released during the tests had mixed with this water. Apparently, each individual aliquot of water was remaining relatively coherent and not mixing with the other water in the subsurface.

There was no evidence of the other isotopic tracers in any of these cores. None of the samples contained isotopic ratios for Sr, Nd, or Pb that were outside of the normal background range. The predicted shift in the $^{87}Sr/^{86}Sr$ ratio (based on the increase in deuterium and bromide) would have been from ~0.715 to >0.79 (depending on the concentration of Sr in the pore water). Clearly, these cations were significantly retarded by sorption and exchange with the sediments.

Table 1. Strontium, Neodymium, and Lead Isotope Data for S-1 (background), S-2, and S-3 Cores. The table includes data collected from the last fiscal year (new or revised data are in bold).

Core	Depth (ft)	Depth (m)[a]	$^{87/86}Sr$[b]	$^{145/144}Nd$[b]	$^{206/207}Pb$[b]	$^{206/208}Pb$[b]
S-1	26-27	8.1			**1.205**	**0.488**
"	32-33	9.9	**0.7140**		**1.200**	**0.484**
"	36-37	11.1			**1.205**	**0.490**
"	38-39	11.7			**1.208**	**0.488**
"	40-41	12.3			**1.204**	**0.491**
S-2	14.0-14.5	4.3			**1.206**	**0.491**
"	18.5-19.0	5.7	0.7147	0.3533		
"	22.5-23.0	6.9	**0.7141**			
"	26.5-27.0	8.2	**0.7153**	0.3498		
"	30.5-31.0	9.4			**1.207**	**0.492**
"	32.5-33.0	10.0	**0.7142**	0.3508	**1.194**	**0.487**
"	36.0-36.5	11.0			**1.210**	**0.488**
"	38.0-38.5	11.7	**0.7139**	0.3495	**1.216**	**0.500**
"	43.0-43.5	13.2	0.7153	0.3517	**1.239**	**0.503**
"	52.5-53.0	16.1	0.7118	0.3515	**1.193**	**0.486**
S-3	18.5-19.0	5.7			**1.198**	**0.487**
"	21.5-22.0	6.6	**0.7141**			
"	25.0-25.5	7.7	**0.7144**			
"	29.0-29.5	8.9	**0.7143**		**1.191**	**0.485**
"	35.0-35.5	10.7	**0.7140**			
"	39.5-40.0	12.1	**0.7138**			
"	52.0-52.5	15.9	**0.7144**			

(a) Depth at midpoint of interval sampled.
(b) Isotope composition in 1:1 mix of sample and de-ionized water.

Analytical Techniques

The cores were collected in lexan tubes and kept sealed and refrigerated until they could be sampled for isotopic analyses. Immediately after splitting open the lexan tubes, approximately 200 g of material were collected from the core material and immediately sealed into plastic sample bottles to prevent evaporation. The pore water in the sediments was then vacuum-distilled from the samples and collected for stable isotope analyses (δD and $\delta^{18}O$). The amount of water in the sediments was determined by comparing the weight before and after the water was distilled from the samples. Then 1:1 mixtures of the dry sediments and de-ionized water were prepared for analyses of the isotopic composition of dissolved solids in the pore water (Sr, Nd and Pb). Bromide concentrations in the cores were measured at PNNL by drying a split of the sample (to determine the water content) and leaching the bromide from the samples with a 1:1 mix of dry sediment and de-ionized water. The bromide concentrations in the leachate were then determined by ion chromatography and calculated back to the actual concentrations in the pore water using the measured water content of the sediments.

Results and Discussion

Borehole WL-2

WL-2 (also known as S-5) was drilled on September 11, 2000, 88 days after the tracer solution was released. The data collected for borehole WL-2 are given in Table 2. The water contents, deuterium, and bromide concentrations for WL-5 are plotted versus depth on Figure 1. The water contents measured by both techniques (vacuum distillation at Lawrence Berkeley National Laboratory [LBNL]/CIG and oven drying at Pacific Northwest National Laboratory [PNNL]) were virtually identical. They are also similar to those observed in the cores studied during FY2001. In general, the water content of the sediments is less than 5% by weight, except in the zone above the less-permeable layers where it increases to 7 to 8%.

Table 2. Data for Samples from WL-2 (S-5) Core Drilled September 11, 2000

Depth (ft)	Depth (m)[a]	%H_2O (Br)[b]	mg/L Br[b]	C/C_o Br	%H_2O (D)[c]	δD (‰)	C/C_o D	$\delta^{18}O$ (‰)	$^{87}Sr/^{86}Sr$[d]
15-16	4.7	2.4	11.33	0.011					
16-17	5.0	2.6	11.12	0.011					
17-18	5.3	2.6	9.61	0.010					
18-19	5.6	3.2	17.06	0.017					
19-20	5.9	4.5	15.07	0.015	4.6	-39	0.031	-16.4	0.7153
20-21	6.2	5.0	6.85	0.007					
21-22	6.6	3.9	2.98	0.003	4.0	-123	0.001	-16.1	
22-23	6.9	5.1	34.47	0.034					
23-24	7.2	8.1	72.02	0.072	7.1	267	0.140	-15.9	0.7158
24-25	7.5	2.7	14.03	0.014					
25-26	7.8	2.7	7.49	0.007					
26-27	8.1	3.0	3.89	0.004					
27-28	8.4	3.4	23.08	0.023					
28-29	8.7	3.5	126.82	0.127	3.3	679	0.287	-16.3	
29-30	9.0	3.5	108.14	0.108					
30-31	9.3	4.1	173.95	0.174	4.3	817	0.336	-16.2	0.7154
31-32	9.6	5.5	146.18	0.146					
32-33	9.9	4.9	166.54	0.167					
33-34	10.2	3.9	150.31	0.150					
34-35	10.5	4.6	60.85	0.061	5.0	105	0.082	-16.0	0.7150
35-36	10.8	5.7	2.74	0.003					
36-37	11.1	5.3	5.48	0.005					
37-38	11.4	6.7	4.37	0.004	7.0	-124	0.001	-15.0	0.7144
38-39	11.7	3.9	5.47	0.005					
39-40	12.0	2.4	5.97	0.006					
40-41	12.3	2.3	8.66	0.009	2.7	-129	-0.001	-15.3	0.7148
41-42	12.6	2.8	4.53	0.005					
42-43	13.0	3.2	4.34	0.004					

Depth (ft)	Depth (m)[a]	%H_2O (Br)[b]	mg/L Br[b]	C/C_o Br	%H_2O (D)[c]	δD (‰)	C/C_o D	$\delta^{18}O$ (‰)	$^{87}Sr/^{86}Sr$[d]
43-44	13.3	2.9	6.02	0.006	2.7	-129	-0.001	-14.9	
44-45	13.6	2.5	7.40	0.007					
45-46	13.9	2.6	7.35	0.007					
46-47	14.2	2.6	4.86	0.005					
47-48	14.5	2.4	7.28	0.007					
48-49	14.8	2.6	4.17	0.004	2.5	-131	-0.002	-14.9	
49-50	15.1	2.4	4.15	0.004					
50-51	15.4	2.5	14.48	0.014					
51-52	15.7	3.3	3.92	0.004	3.4	-128	-0.001	-15.3	
52-53	16.0	3.3	3.60	0.004					
53-54	16.3	3.3	3.98	0.004					
54-55	16.6	4.2	4.61	0.005	4.3	-125	0.001	-15.8	
55-56	16.9	3.8	6.45	0.006					
56-57	17.2	2.4	6.80	0.007					
57-58	17.5	2.4	8.26	0.008	2.7	-131	-0.002	-14.6	
58-59	17.8	2.3	4.90	0.005					
59-60	18.1	2.5	5.26	0.005					

(a) Depth in meters at midpoint of sampled interval.
(b) Percent water (%weight of water in sample) and bromide concentrations for bromide samples determined at PNNL.
(c) Percent water (%weight of water in sample) for deuterium samples determined at LBNL/CIG.
(d) Isotope composition in 1:1 mix of sample and de-ionized water.

The deuterium and bromide concentrations in the samples show similar trends to those observed in boreholes S-2 and S-3. There is some increase in concentration above the upper less-permeable layer, but the peak concentrations are located 1 to 2 m above the lower less-permeable layer. There are, however, two notable differences between the data from WL-2 and that collected for S-2 and S-3. The degree of enrichment for both deuterium and bromide is less for WL-2. Also, the bromide data peaks at significantly lower concentrations than the deuterium (~17% for bromide versus ~34% for deuterium). In general, the deuterium concentrations are about twice as high as the bromide concentrations throughout the core.

The leak fluids also shifted the $\delta^{18}O$ values of the pore waters. Although the $\delta^{18}O$ values of the leak fluids were not intentionally altered, there was a large enough difference between the leak waters and the pore waters to detect the leak fluids. The $\delta^{18}O$ value of the porewater was initially approximately -15‰, whereas the leak waters were about -17‰. This difference facilitates a comparison between infiltration of all the leak fluids relative to that of the tracer fluids alone.

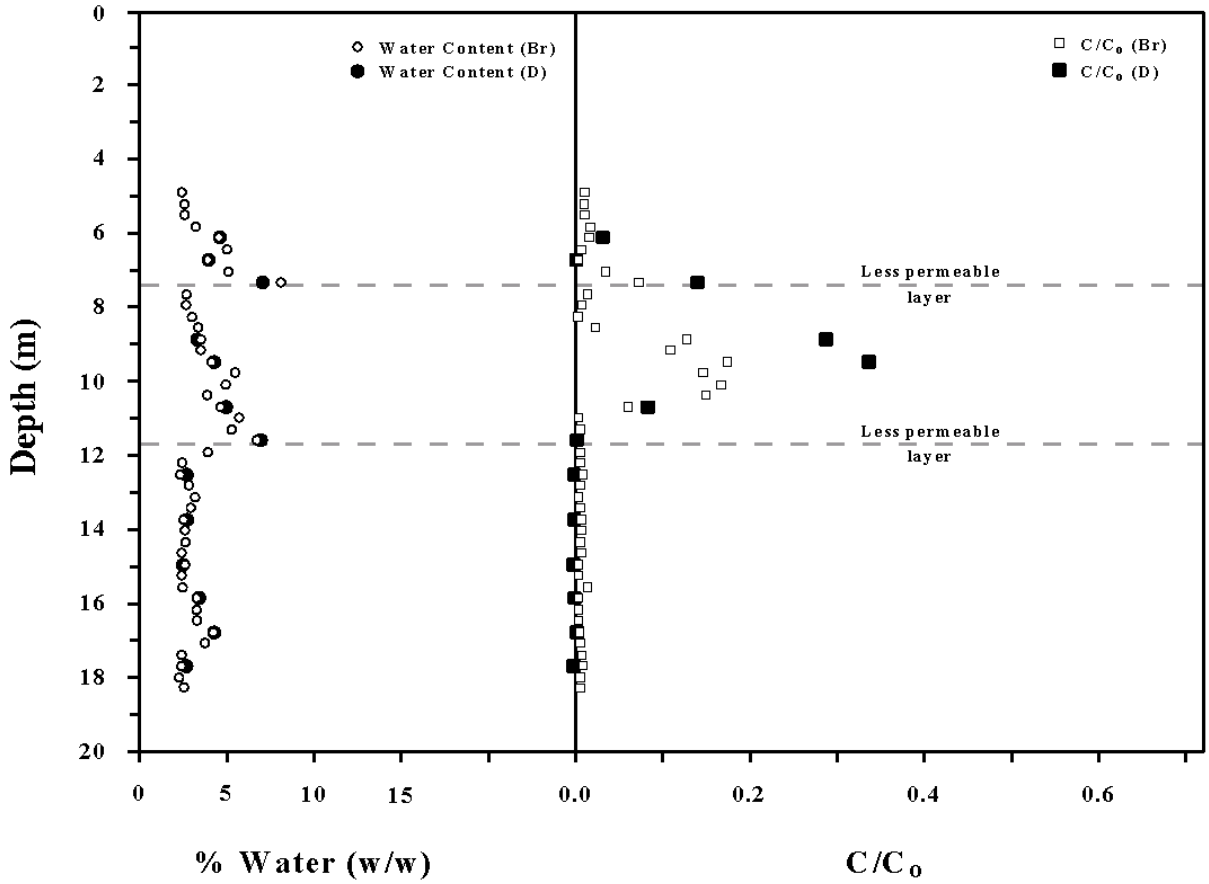

Figure 1. Water Contents Determined for Both Bromide and Deuterium Samples from Borehole WL-2 (S-5) Plotted on Right; Concentrations of Deuterium and Bromide Relative to Their Initial Concentrations (C_o) in Tracer Solution Plotted on Left. Also shown are the approximate depths of the less-permeable layers in the sediments (determined from the measured water contents and the results of geophysical studies at the site).

Basically, the results for $\delta^{18}O$ were similar to those observed for deuterium and bromide. The largest shifts in the $\delta^{18}O$ values of the pore water in WL-2 were directly above the upper less-permeable layer and in the zone between the two less-permeable layers. The high-water-content sediments just above the lower less-permeable layer and beneath that layer were not significantly shifted. However, at 6 to 8 m in depth in WL-2 where there was little evidence of the deuterium, the $\delta^{18}O$ values of the pore water are significantly below background. This is consistent with the results for the S-2 and S-3 cores, where the $\delta^{18}O$ values of the pore water samples indicated that the non-tracer leak fluids had interacted with more of the sediments than the tracer solution.

The $^{87}Sr/^{86}Sr$ ratios of six samples from this hole have been analyzed. These samples include all of the samples with significantly elevated deuterium concentrations ($C/C_o > 0.01$). The Sr isotope ratios for

these samples were slightly higher than the average background ratio (by <0.001), but were all still within the background range.

Boreholes WL-3A and WL-4

WL-3A (also known as S-7) and WL-4 (also known as S-8) were drilled on March 23, 2001, 281 days after injection of the tracer solution and 1 week before release of the Na-thiosulfate solutions began. WL-3A was drilled ~3.5 m from the injection well, and WL-4 was drilled ~8 m from the injection well. The data collected for these two boreholes are given in Table 3. The water contents, deuterium, and bromide concentrations for WL-3A are plotted versus depth on Figure 2. The water contents were only measured for the isotope samples (by vacuum distillation at LBNL/CIG), so those water contents had to be used to correct the bromide concentrations.

The bromide and deuterium concentrations in WL-3A peaked at about the same depth as in the earlier boreholes (approximately midway between the two less-permeable layers). However, the relative concentration of bromide was only about 25% of the deuterium concentration. For WL-4, the deuterium and bromide concentrations peaked at 11.4 m in depth. The highest deuterium concentration in WL-4 is about 25% of the highest deuterium concentration in WL-3A. This is expected, given that WL-4 is roughly twice as far from the injection well as WL-3A. However, the peak concentration of bromide in WL-4 is higher than the peak bromide concentration in WL-3A. There were additional measurements of bromide in 1:1 leach solutions, which were all less than the concentration measured at 11.4 m, but no water content data were available to correct those concentrations back to the pore-water concentrations. The reason for the high bromide in WL-4 is not clear. Possible explanations include pre-existing bromide from earlier tracer studies or laboratory analytical errors.

The $^{87}Sr/^{86}Sr$ ratios of pore waters from the samples from the WL-3A core with elevated deuterium concentrations were analyzed (Table 3). There is no indication of the high $^{87}Sr/^{86}Sr$ in the tracer solution. In fact, the slight increase over the average background observed in the $^{87}Sr/^{86}Sr$ ratios from WL-2 is not duplicated in this data (suggesting that the signal in WL-2 was probably just a slightly higher background?).

Table 3. Data for samples from WL-3A (S-7) and WL-4 (S-8) cores drilled March 23, 2001

Core	Depth (ft)	Depth (m)[a]	$\%H_2O$[b]	C/C_o Br[c]	δD (‰)	C/C_o D	$\delta^{18}O$ (‰)	$^{87}Sr/^{86}Sr$[d]
WL-3A	19-20	5.9	4.1	0.003	-69	0.020	-17.0	0.7148
“	26-27	8.1	2.9	0.021	96	0.079	-17.7	0.7143
“	29-30	9.0	3.2	0.067	568	0.247	-17.1	0.7141
“	33-34	10.2	5.1	0.029	244	0.132	-16.3	0.7145
“	36-37	11.1	6.6	0.002	-101	0.009	-15.4	
“	37-38	11.4	5.7	0.001	-123	0.001	-15.3	0.7144
“	44-45	13.6	3.0		-132	-0.002	-15.4	0.7142
“	49-50	15.1	3.4		-132	-0.002	-15.3	0.7145
“	54-55	16.6	2.8		-134	-0.003	-15.3	
WL-4	20-21	6.2	4.1	0.000	-121	0.002	-13.9	

Core	Depth (ft)	Depth (m)[a]	%H_2O[b]	C/C_o Br[c]	δD (‰)	C/C_o D	$\delta^{18}O$ (‰)	$^{87}Sr/^{86}Sr$[d]
"	37-38	11.4	8.7	0.097	45	0.061	-14.6	
"	43-44	13.3	3.0		-106	0.007	-16.0	

(a) Depth at midpoint of interval sampled.
(b) Percent weight of water of total weight of sample.
(c) Bromide concentrations measured at PNNL.
(d) Isotope composition in 1:1 mix of sample and de-ionized water.

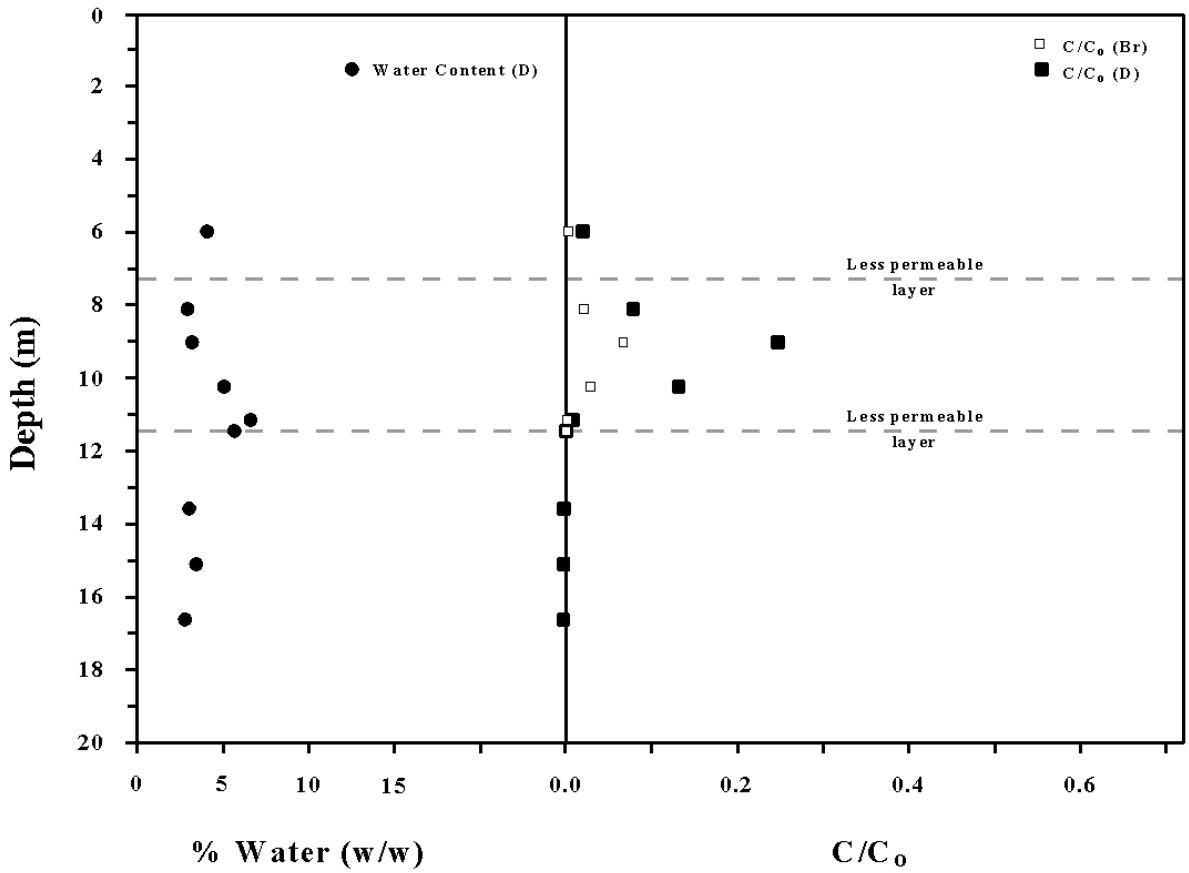

Figure 2. Water Contents Determined for Deuterium Samples from Borehole WL-3A (S-5) Plotted on Right; Concentrations of Deuterium and Bromide Relative to Their Initial Concentrations (C_o) in the Tracer Solution on Left. Also shown are the approximate depths of the less-permeable layers in the sediments (determined from the measured water contents and the results of geophysical studies at the site).

Boreholes WL-7 and WL-10

Pore-water samples have been extracted from two of the cores drilled after injecting the Na-thiosulfate solution (WL-7 ad WL-10). The data measured for these waters are given in Table 4 along with analyses of δD and $\delta^{18}O$ values of water distilled out of a sample of the Na-thiosulfate solution. The isotope data for these samples are also plotted on Figure 3. Most of the samples from WL-7 and WL-10 fall within the range of values bounded by Columbia River water (the primary source of the leak fluids), the average pore water from the 299-W22-48 ("clean" core), and the tracer solution. The only samples that appear to be significantly enriched in deuterium are the two samples from 9.0 and 10.2 m depth in WL-7. This is the same depth as the peak deuterium in the boreholes drilled before the Na-thiosulfate was leaked into the ground. The maximum degree of enrichment of deuterium (C/C_o ~5%) is considerably lower than in the earlier cores, but this depth also corresponds to the section of the core with the highest concentration of Na-thiosulfate. Apparently, the Na-thiosulfate solutions mixed with the deuterium tracer solution, but did not displace it.

Table 4. Data for Samples from WL-7 (drilled 5/9/01) and WL-10 (drilled 5/23/01) Cores

Core	Depth (ft)	Depth (m)[(a)]	$\%H_2O$[(b)]	δD (‰)	$\delta^{18}O$ (‰)
Thiosulfate solution	-	-	3.1	-91	-13.3
WL-7	18-19	5.6	7.7	-108	-15.8
"	23-24	7.2	6.8	-113	-15.6
"	29-30	9.0	6.3	26	-10.5
"	33-34	10.2	5.3	67	-10.7
"	37-38	11.4	6.3	-122	-14.7
"	39-40	12.0	2.8	-122	-14.8
"	48-49	14.8	3.1	-124	-14.4
WL-10	19-20	5.9	10.2	-126	-17.4
"	23-24	7.2	3.8	-121	-16.9
"	28-29	8.7	5.0	-104	-14.8
"	33-34	10.2	5.3	-109	-14.8
"	35-36	10.8	5.4	-72	-11.0
"	38-39	11.7	7.0	-73	-12.1
"	40-41	12.3	4.0	-96	-14.7
"	45-46	13.9	3.5	-119	-15.1
"	54-55	16.6	3.1	-124	-14.4

(a) Depth at midpoint of interval sampled.
(b) Percent weight of water of total weight of sample.

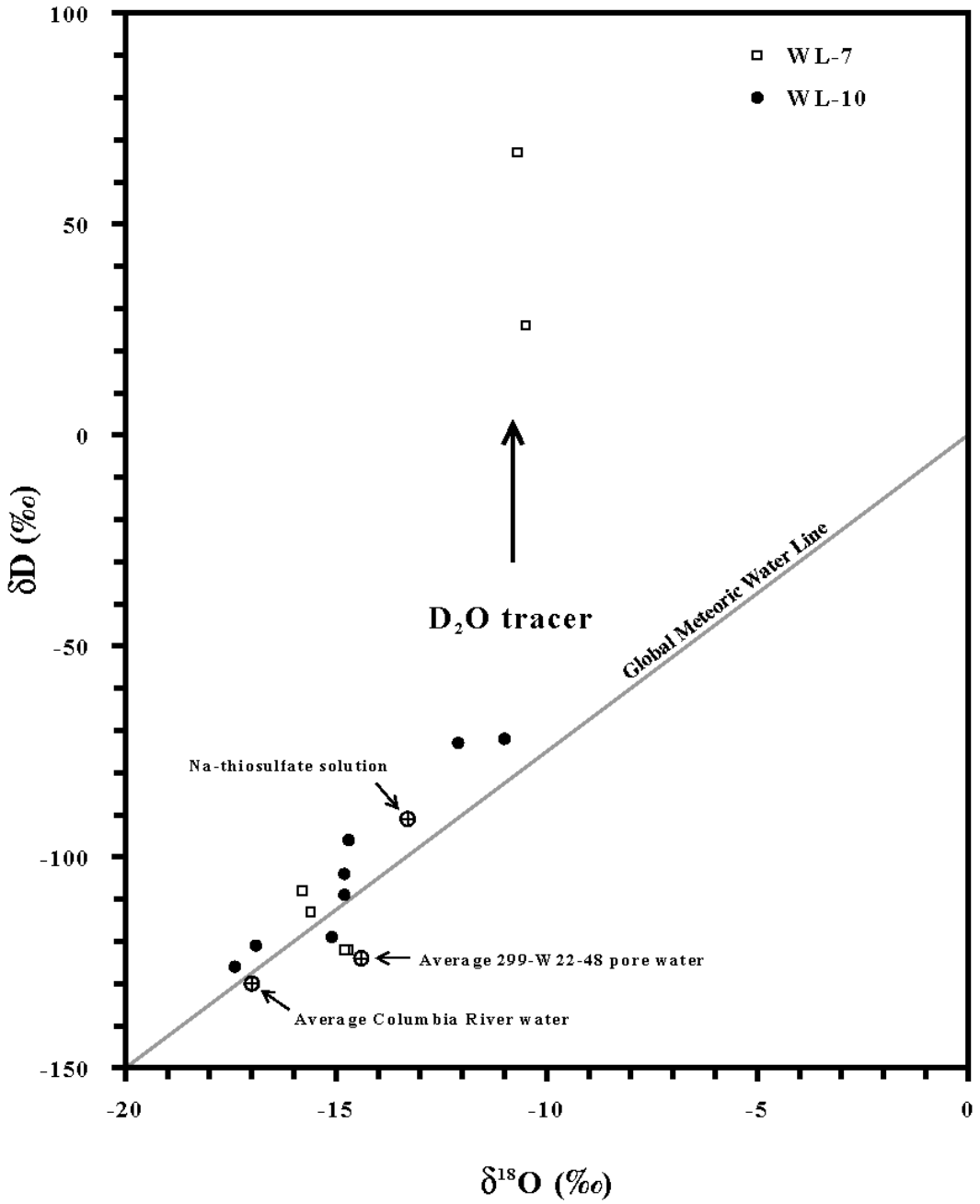

Figure 3. Plot of Oxygen and Hydrogen Isotope Compositions of Pore Water Samples Extracted from WL-7 and WL-10 Cores Drilled at Sisson and Lu Site after Injecting Na-Thiosulfate Solution. Most of the samples fall within the range of compositions bounded by the compositions of Columbia River water (the source of water for the injection fluids), the background pore waters (defined by the average of the compositions measured for the 299-W22-48 pore water), and a sample of the Na-thiosulfate solution. The only samples significantly enriched in deuterium were from 9.0 and 10.2 m in the WL-7 core (the same depth as the peak deuterium concentrations measured before injecting the Na-thiosulfate solution).

Comparison of the Deuterium and Bromide Results

The change over time in the peak deuterium and bromide concentrations in the boreholes drilled between 3 and 4 m from the injection well is shown on Figure 4. There are two sets of points plotted for S-3 because the deuterium peak was at a different depth than the bromide peak. The trends drawn on the figure start at the average value for the S-2 and S-3 concentrations and extend through the WL-2 and WL-3A points. This figure clearly demonstrates the difference in behavior between the two tracers. The reason for the faster decrease in bromide is not clear at this time.

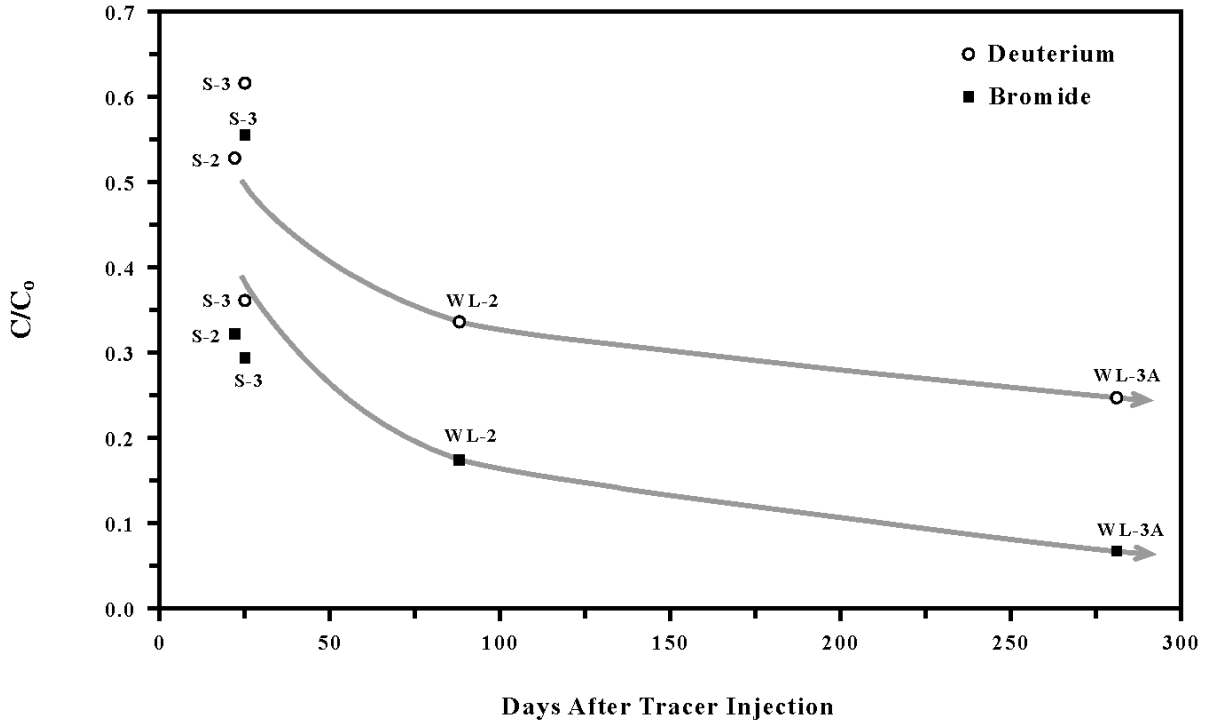

Figure 4. Plot of Peak Concentrations Versus Time of Deuterium and Bromide in Boreholes Drilled Between 3 and 4 m from Injection Well at Sisson and Lu Site. The labels on the data points are the boreholes from which the data were collected. There are two pairs of points for S-3 because the deuterium and bromide peaks occurred at different depths. The trend lines plotted on the figure begin at the average values for the S-2 and S-3 data and extend through the additional data.