STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Processing of Diffusion Samplers to Test Remediation of Uranium by Humate

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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ABSTRACT

Savannah River Site (SRS) was one of the major U.S. Department of Energy (DOE) facilities that served as a defense nuclear processing facility during the Cold War era. From 1955 to 1988, the SRS F-Area seepage basins received approximately 1.8 billion gallons of low level waste solutions containing harmful contaminants due to plutonium separation operations. Previous studies have shown humic acid to be a potential approach for controlling contaminant mobility. At mildly acidic pH, humic acid sorbed to sediments is expected to strongly bind with uranium, and potentially iodine-129 (I-129), allowing stabilization of the contaminant.

During this internship, diffusion samplers deployed in existing F-Area wells were processed to further test the effects of sorption of uranium by humate-loaded sediments. The aqueous and solid phases for each sampler were separated and analyzed for uranium and tritium. Results of tritium concentrations indicated diffusion samplers were effective in reaching chemical equilibrium with groundwater, thus solutes had the capability to diffuse through. Uranium analyses found higher concentration of humate lead to a decrease in aqueous uranium concentrations and an increase in sorption to sediment, determined by the uranium distribution coefficient. It was also noted that humate was still sorbed to sediment after the deployment period which provides some insight to the longevity of humate as a treatment. Future work involves analyzing samplers for I-129 and total organic carbon.

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1. INTRODUCTION

Savannah River Site (SRS), located in Aiken, South Carolina, was one of the major U.S. Department of Energy (DOE) sites that served as a defense nuclear processing facility during the Cold War. From 1955 to 1988, SRS produced plutonium and irradiated fuel in the F-Area Separations Facility, generating large amounts of radioactive and acidic waste. The unlined F-Area seepage basins received approximately 1.8 billion gallons of low-level waste solutions that evaporated and seeped into underlying soil. The purpose of the basins were to keep contaminants from migrating by binding with the soil, however acid and the most mobile radionuclides, uranium isotopes, strontium-90 (Sr-90), iodine-129 (I-129), technetium-99 (Tc-99) and tritium (H-3) migrated into the groundwater, creating an acidic plume of pH between 3 and 5.5.

Since the 1950s, there has been monitoring and assessment of the groundwater, and even after remediation efforts, groundwater remained acidic, with a pH of 3.2 around the basins to a pH of 5 downgradient. In 1997, pump-and-treat and re-injection systems were applied to remove the harmful contaminants in groundwater. Downgradient groundwater was pumped to a water treatment facility to remove metals, and reinjected up-gradient within the aquifer. Eventually this method became less effective as generation of radioactive waste increased along with costs to maintain. In 2004, the pump-and-treat and re-injection systems were replaced by a funnel and gate system. This system created a treatment zone through the injection of a solution mixture composed of sodium hydroxide and carbonate to raise the pH levels in the F-area. The treatment zone was expected to reverse the acidic nature of contaminated sediments, creating a more negative charge on the surface of sediment particles, thus enhancing adsorption of cationic contaminants. A systematic re-injection of the base was required to raise the pH to near neutral values. The continuous use of high concentrations of a carbonate solution caused a concern of possible remobilization of uranium that had previously adsorbed in the treatment zone, since U (VI) forms soluble aqueous uranyl-carbonate complexes in the presence of bicarbonate ions.

Savannah River National Lab (SRNL) has been testing an unrefined, inexpensive humate amendment, known as Huma-K, to enhance sorption of uranium, Sr-90, and I-129 when injected into contaminated plumes. Humic substances are ubiquitous in the environment, occurring in all soils, waters, and sediments of the ecosphere. They are complex organic compounds developed by humification, the process of decomposition of plant and animal tissue. In humification, organic matter is naturally transformed by microorganisms in the soil.

Humic substances are divided into humic acid, fulvic acid, and humin, varying in solubility. Humic acids are extractable with alkali and precipitate with acid; fulvic acids are extractable with alkali and soluble in acid; and humin is not extractable with alkali (Gray and Williams, 1971). The three components also vary in molecular weight, elemental composition, structure, and number and position of functional groups.

In this study, Huma-K was used in place of refined humic acid and includes high humic and fulvic compounds that come from the alkaline extraction of leonardite. It was developed for farmers as an organic fertilizer to encourage plant growth and nutrient uptake on a large scale.

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In 2013, SRNL performed a field test of humic acid technology for uranium and I-129 at the F-Area Field Research Site (FRS) using Huma-K. The studies conducted during this internship as well as other sorption studies conducted with humate and uranium will contribute to understanding the mechanisms, feasibility and potential applicability of this humate injection technology for remediation of uranium contamination in the environment.

2. EXECUTIVE SUMMARY

3. RESEARCH DESCRIPTION

In this study, diffusion samplers deployed in SRS's F-Area (Figure 1) were processed to further test the effects on sorption of uranium by humate-loaded sediments. Diffusion samplers used consisted of glass vials with screw-on caps and washer-like septa to hold glass fiber filter paper, which separated the inside contents from the environment. Each vial contained approximately 15 g of sediment from subsurface core FAW-1 81'-83', pre-equilibrated with different concentrations of humate solution and pH adjusted to ~3.5 using hydrochloric acid, HCl. Samples were tested in triplicate at low (50 ppm), middle (150 ppm) and high (300 ppm) concentrations respectively for each well. Excess humate solution from each concentration was used to fill the remainder of the respective vials. In addition, sediment samples with no humate and blank water samples were deployed, serving as controls. An advantage of using the diffusion sampler method is elimination of the need for construction of new wells or sampling of groundwater, as the samplers are placed directly inside existing monitoring wells.
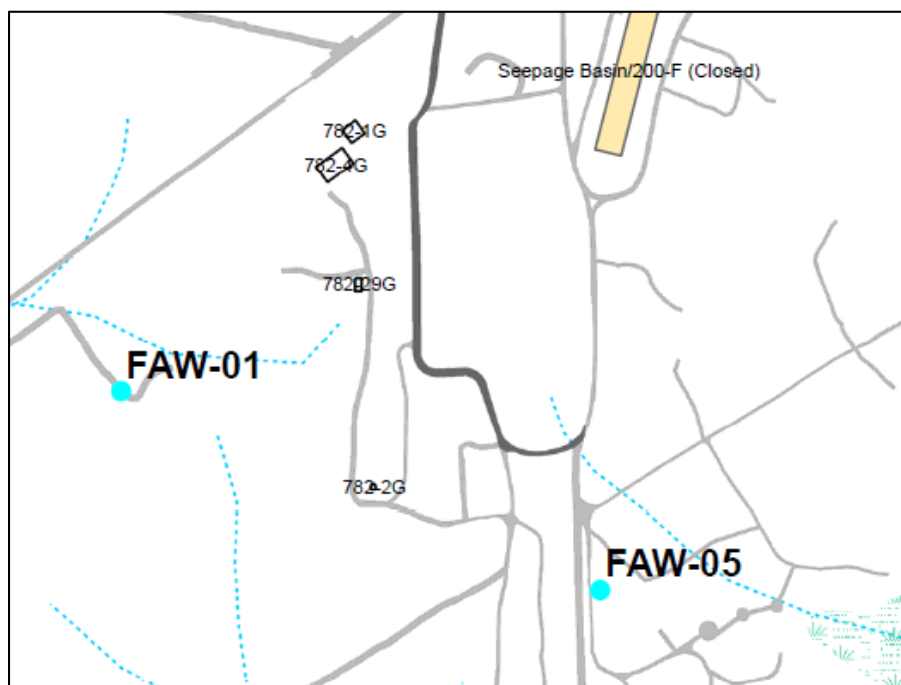
Figure 1: Map of deployment wells in F-Area.

Field Deployment

Prior to deployment, field parameter profiles for wells FAW-1, uncontaminated, and FAW-5, contaminated, were conducted to determine the optimal depth for the samplers. The target zone was where pH was low, as more sorption is expected to occur at low pH, and also where specific conductivity was high, as greater specific conductivity indicates greater ionic constituents and high concentrations of uranium. As shown in Figure 2, the target zone for FAW-5 was between 62'-66' below the reference casing and at pH ~ 3.2. The target zone for FAW-1 was between 84'-88' below the reference casing, at pH ~ 4.5.
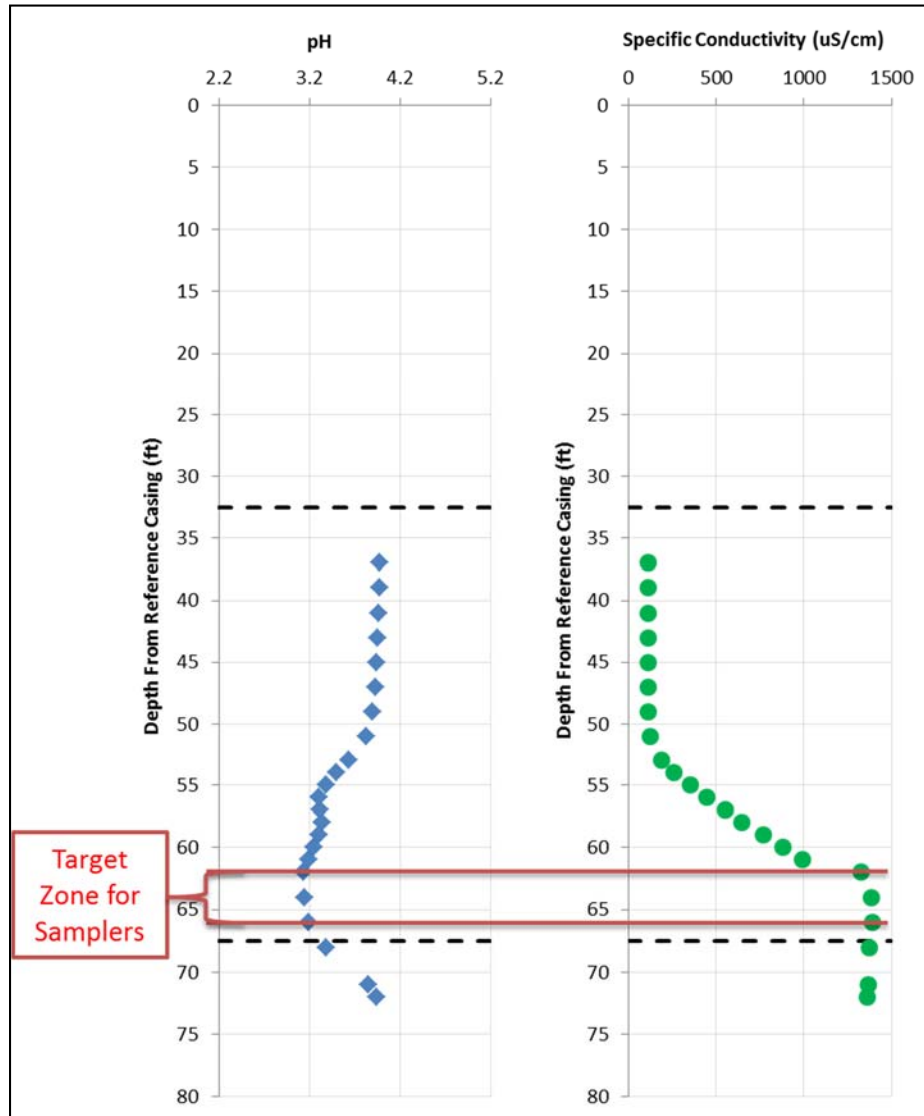
Figure 2: Depth profile of FAW-5.

Prior to deployment, the target zone was used to measure out wire to attach the 4 levels of plastic tube netting where diffusion samplers would be placed. The netting was fastened to the wire with plastic zip ties, with the other end left open to place samplers in once in the field at the well. A stainless steel weight was attached to the end of the wire to rest on the bottom of the well to counteract the buoyancy of materials. The top of the wire was attached to the well cap, and securely wound around a nearby metal stake (see Figure 3, Figure 4 and Figure 5).
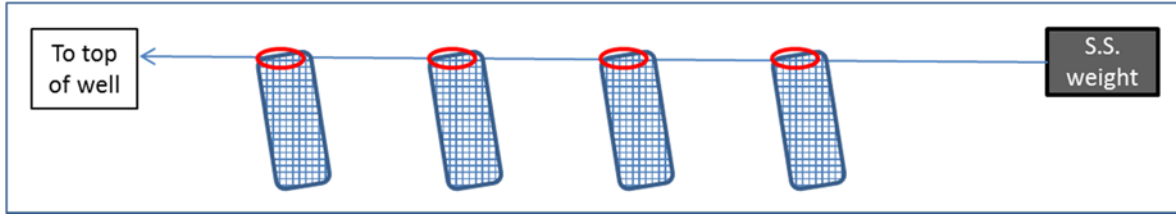
Figure 3: Deployment of samplers in well (not to scale).

Samplers were left in wells to equilibrate with the groundwater for approximately 5 months; once retrieved, they were placed in the refrigerator at 4°C until they were processed. This experiment will observe if the sorption of uranium and iodine-129 varies for different initial concentrations of sorbed humate. The experiment will also look at desorption of humate in actual groundwater conditions.

Figure 4: Samplers in plastic mesh.

Figure 5: Sampler retrieval.

During this internship, diffusion samplers that were deployed were prepped and processed to study the sorption of uranium (Figure 6). The research performed consisted of separating the aqueous and solid phases for each sampler, and processing the groundwater, pore water, and sediment for analyses. The groundwater was processed to test for uranium, tritium, and I-129. The pore water of the samplers was processed to test for uranium, and the sediment was processed to test for extracted uranium and total organic carbon (TOC).
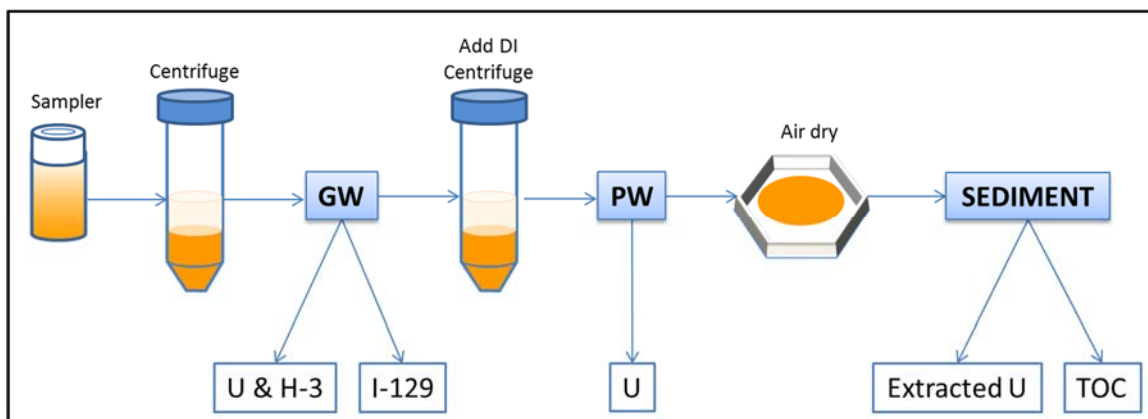
Figure 6: Processing of a diffusion sampler.

Experimental Methods

The contents of samplers were initially swirled to mix sediment and groundwater, then emptied into 50-mL plastic centrifuge tubes. A spatula was used to scrape any remaining sediment into the vial (Figure 7). Some liquid was also poured from the tube back into the vial to loosen particles adhered to the walls and then poured back into its tube. The tubes were centrifuged at 4000 rpm for 10 minutes, using a Fisher Scientific Marathon 8K Benchtop Centrifuge, until the liquid portion was clear (Figure 8). The supernatant (~15 mL) was poured off and split into two sub-samples in 20 mL Nalgene vials. The first sub-sample was acidified with 0.5 mL of 0.1 N HNO_3 to adjust the pH to 2-3 in order to preserve uranium for analysis (verified by litmus paper). The second sub-sample was reserved for analyzing for I-129.
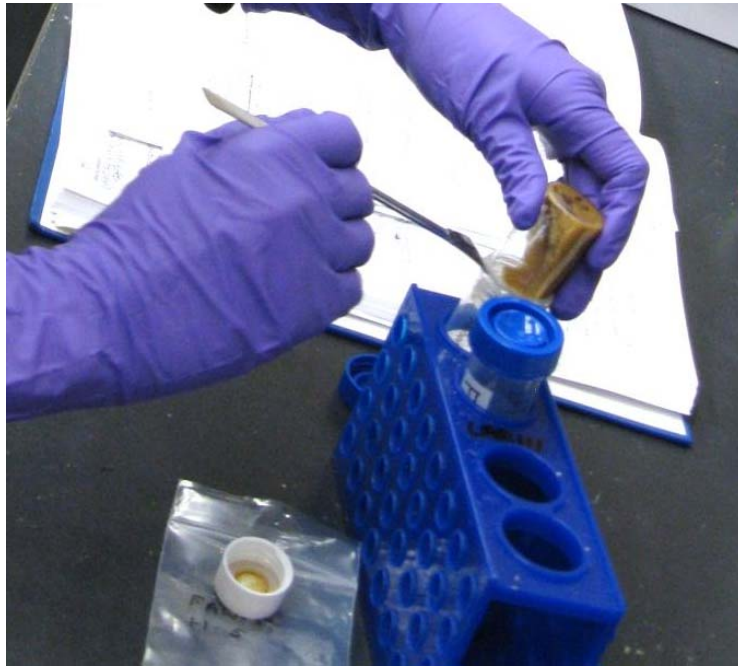
Figure 7: Emptying diffusion sampler.

Figure 8: Contents of sampler centrifuged.

The centrifuge tubes left with sediment had 20 mL of DI water added to them. A glass stirring rod was used to gently mix the sediment with DI water and minimize sediment adhering to the wall. The mixture was centrifuged for 10 minutes, or until clear. The supernatant was poured into

20 mL Nalgene vials and excess liquid was discarded. These pore water samples were acidified with 0.5 mL of 0.1 N HNO_3 for preservation.

The sediment remaining in the centrifuge was analyzed for extracted uranium and TOC. Sediments were scooped out of the tubes onto plastic weighing boats and allowed to air dry overnight (Figure 9). The centrifuge tube was also left to dry, to scrape any remaining sediment from the tube onto the boat the following day. Once dried, a pestle was used to gently disaggregate the sediment. It was then split into two samples, one for TOC analysis, ~5 g, and one for extractions, ~10 g.


Figure 9: Sediments air drying.

Uranium Extractions

A sodium bicarbonate/carbonate solution was prepared to extract uranium from dried sediments, following Kohler et al. (2004). A total of 3 L of $1.44 \cdot 10^{-2}$ M $NaHCO_3$ and $2.8 \cdot 10^{-3}$ M Na_2CO_3 was prepared, with a pH of 9. The solid-to-liquid ratio used was 50 g/L. The sediment allocated for extractions was transferred to glass Erlenmeyer flasks, where the weight of sediment was recorded. After adding the appropriate amount of extraction solution, flasks were placed on a Thermo Scientific MaxQ 2508 shaker table to vigorously mix for 5 days, and settle for 1 day (Figure 10). Supernatant was poured off into 20 mL Nalgene bottles. To samples that did not settle, 20 mL of the top liquid was pipetted into tubes to centrifuge, and then poured off into bottles. These samples were submitted for U analysis. All samples collected for uranium analyses were analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

Figure 10: Extractions on shaker table.

Table 1: Analysis Matrix

Sample ID	Well	Sediment Equilibrated w/ Humate	GROUNDWATER ANALYSES			POREWATER ANALYSES	SEDIMENT ANALYSES	
			Uranium	Tritium	I-129	Uranium	Extracted Uranium	TOC
BW1	FAW1	none	X	X	X	X	no analysis needed (no sediment in sample)	
BW2	FAW1	none	no analysis needed					
BW3	FAW5	none	X	X	X	X		
BW4	FAW5	none	no analysis needed					
BS1	FAW1	none	X	X	X	X	X	X
BS2	FAW1	none	X	X	X	X	X	X
BS3	FAW1	none	no analysis needed					
BS4	FAW5	none	X	X	X	X	X	X
BS5	FAW5	none	X	X	X	X	X	X
BS6	FAW5	none	no analysis needed					
L1	FAW1	low conc; 50 mg/L Huma K	X	X	X	X	X	X
L2	FAW1	low conc; 50 mg/L Huma K	X	X	X	X	X	X
L3	FAW1	low conc; 50 mg/L Huma K	X	X	X	X	X	X
L4	FAW5	low conc; 50 mg/L Huma K	X	X	X	X	X	X
L5	FAW5	low conc; 50 mg/L Huma K	X	X	X	X	X	X
L6	FAW5	low conc; 50 mg/L Huma K	X	X	X	X	X	X
M1	FAW1	middle conc; 150 mg/L Huma K	X	X	X	X	X	X
M2	FAW1	middle conc; 150 mg/L Huma K	X	X	X	X	X	X
M3	FAW1	middle conc; 150 mg/L Huma K	X	X	X	X	X	X
M4	FAW5	middle conc; 150 mg/L Huma K	X	X	X	X	X	X
M5	FAW5	middle conc; 150 mg/L Huma K	X	X	X	X	X	X
M6	FAW5	middle conc; 150 mg/L Huma K	X	X	X	X	X	X
H1	FAW1	high conc; 300 mg/L Huma K	X	X	X	X	X	X
H2	FAW1	high conc; 300 mg/L Huma K	X	X	X	X	X	X
H3	FAW1	high conc; 300 mg/L Huma K	X	X	X	X	X	X
H4	FAW5	high conc; 300 mg/L Huma K	X	X	X	X	X	X
H5	FAW5	high conc; 300 mg/L Huma K	X	X	X	X	X	X
H6	FAW5	high conc; 300 mg/L Huma K	X	X	X	X	X	X

The sample ID's in Table 1 indicate: BW- water blank, BS- blank sediment, L-low concentration, M-middle concentration, and H-high concentration.

4. RESULTS AND ANALYSIS

During deployment, diffusion samplers were subject to changes in the chemical composition of its contents as they equilibrated with groundwater in wells. Results from tritium analysis would indicate whether or not chemical equilibrium with groundwater actually occurred within diffusion samplers. In FAW-5, samplers were expected to have some concentration of tritium; otherwise diffusion may not have occurred. Results showed concentrations of H-3 in groundwater samples to be slightly above the average H-3 level from the past 2 years of a nearby well, FSB-126D. The average concentration for FSB-126D was 1280 pCi/mL, while results were between 1600-2000 pCi/mL.

The reason concentrations are likely to be slightly lower at well FSB-126D is because samples collected there are the composite of all the water that flows through the screen zone. The acidic plume in F-Area runs vertically and does not cover the entire screen zone, therefore the samples of this well are diluted with cleaner water, having lower concentrations of H-3. Analyses were not performed on FAW-1, as significant concentrations of H-3 are not expected to be present in this uncontaminated well.
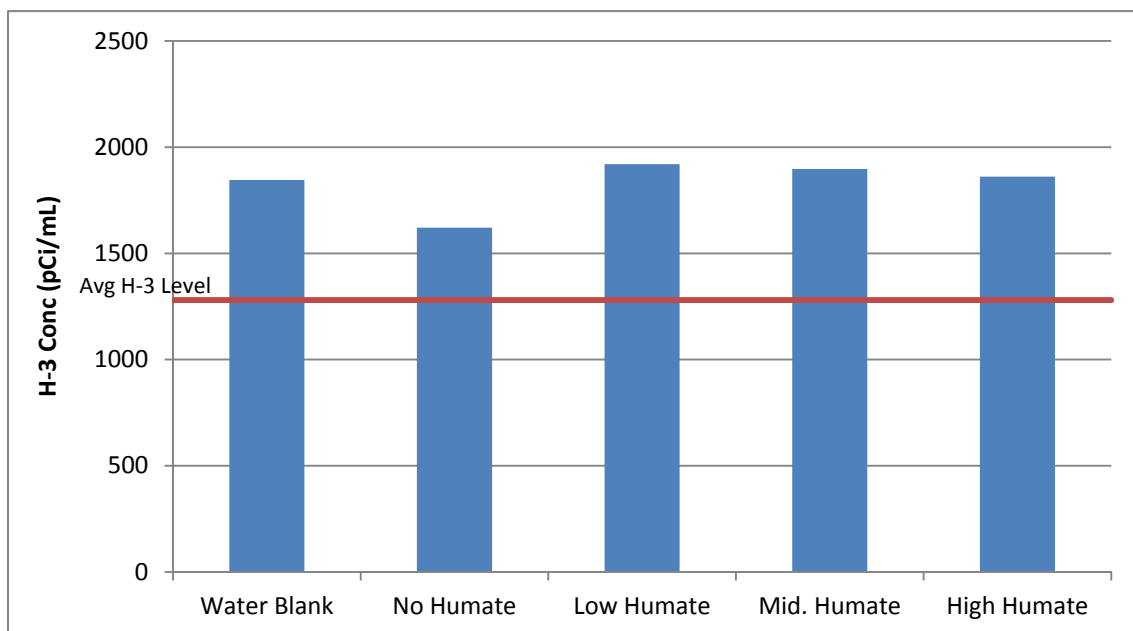
Figure 11: Concentrations of Tritium in FAW-5 with varying humate concentrations.

Table 2 displays the average concentrations of uranium, in μg/L, in all samples for each well and phase of sampler, organized by concentration of humate. In FAW-5, aqueous U concentrations decreased with humate concentration, with pore water following the same trend. The purpose of performing the sodium bicarbonate/carbonate extractions was to desorb the U (VI) from the surfaces of sediment since U (VI) forms strong aqueous complexes with carbonate. The extracted concentrations for FAW-5 seemed to have increased with humate concentration, although this had some variability. The standard deviations observed in Table 2 indicate there was significant

variability in some of the samplers. A possible explanation for this is the configuration in which they were placed in the wells, since samplers were spanned out in four levels of placement in the target zone.

In FAW-1, aqueous U concentrations showed a slight increase and extracted concentrations decreased beginning from the low humate concentration, but overall this was not too significant since concentrations were very low to begin with.

Table 2: Uranium Measurements* for Diffusion Samplers in μg/L

	FAW-5				FAW-1			
	no humate	low humate	mid. humate	high humate	no humate	low humate	mid. humate	high humate
GW	509 ± 68	421 ± 81	265 ± 43	162 ± 86	0	2 ± 1	6 ± 4	7 ± 5
PW	206 ± 7	130 ± 20	80 ± 10	44 ± 1	0	5 ± 5	3 ± 2	17 ± 11
Extracted	77 ± 5	207 ± 27	214 ± 20	210 ± 65	12	25 ± 8	19 ± 1	16 ± 7

*Average concentration $\pm$ standard deviation

Uranium Distribution Coefficient

In remediation studies, a significant parameter to determine is the distribution coefficient, K_D, which describes the partitioning of uranium between the solid and aqueous phases. The uranium distribution coefficient is calculated as the concentration of sorbed U(VI) to sediment divided by the dissolved uranium concentration in groundwater extracted from the diffusion sampler. The concentration of sorbed U(VI) is determined using the mass of uranium from sediment extractions divided by the mass of sediment in each flask.

$$K_D = \frac{\text{Sorbed U Concn } (\frac{mg}{kg})}{\text{Dissolved U Concn } (\frac{mg}{L})}$$

The uranium distribution coefficients found in diffusion samplers deployed in FAW-5 were significantly smaller than in FAW-1, as shown in Figure 12. This would indicate that greater sorption took place in FAW-1 samplers, however masses of uranium were very low and is likely inconsistent. A possible reason for the differences could also be caused by the different pH values of the media in which the samplers were placed. In FAW-5 samplers were deployed in pH 3.2, while in FAW-1 samplers in pH 4.5.

It should also be noted that while processing, there was difficulty in getting FAW-1 water samples to settle, even after centrifuging twice. Some samples sent for analyses had color and slight cloudiness that could have contributed to minor errors in results. The samples that were distinctly different were recorded and were not included in concentration averages if they resulted in significant discrepancies from similar sample results.

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For samplers deployed in FAW-5, the distribution coefficients increased with increased concentration of humate, a positive sign because this indicates that more sorption occurred for higher concentrations of sorbed humate used.

For samplers deployed in FAW-1, the distribution coefficients did not have a consistent trend with increased humate concentration, which could have probably been predicted from Table 2 results. This is likely due to the concentrations of uranium in the samples being very low, some under the detectable limit, and therefore inconsistent.
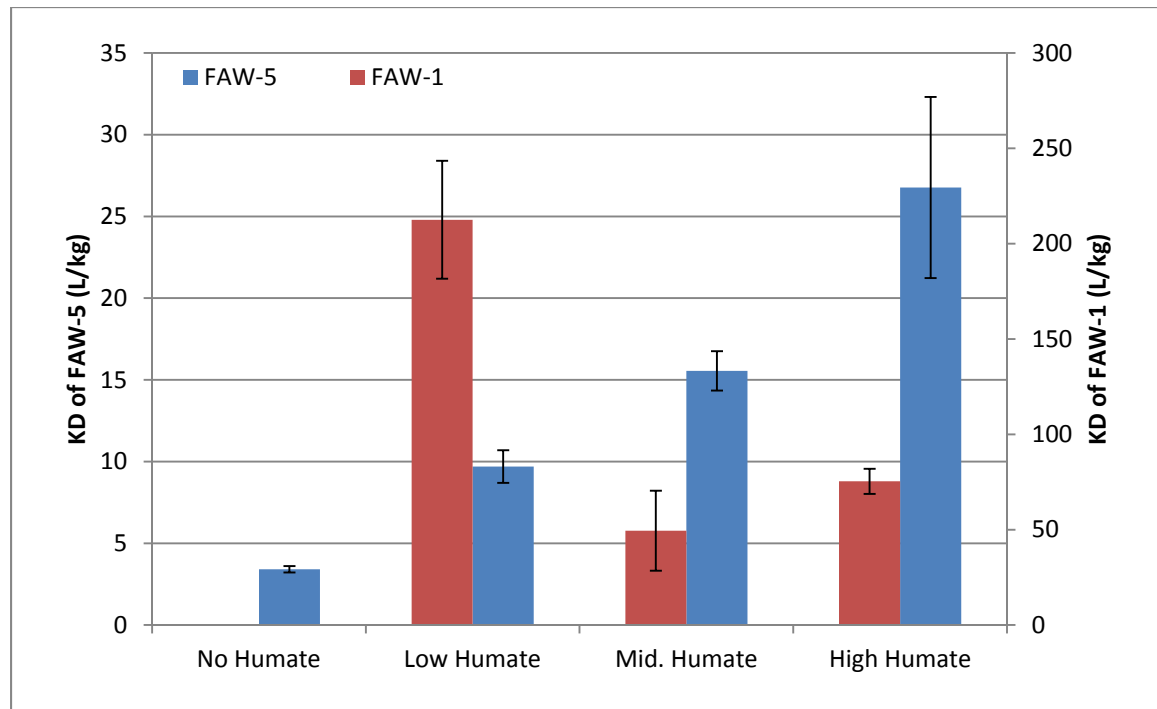

Figure 12: Distribution coefficients, K_D, of uranium.

By comparing the data for FAW-5, it is noticed that with increasing humate concentration, the concentration of dissolved U decreases, while the distribution coefficient increases. This data indicates the rate of uranium sorption to the diffusion sampler sediments is greater than the rate of uranium diffusion into the sampler.

In addition to these results, the amount of humate that desorbed in actual groundwater conditions was also important to analyze. The humate did not completely desorb during its time in the wells and demonstrated that it was still effective after 5 months when samplers were retrieved, as uranium remained sorbed to sediment. Also, the color of some of the extracted samples suggested that humate was still present. This indicates that there is some longevity of humate to be considered for actual humate field injections and use as a treatment.

5. CONCLUSION

Diffusion samplers have shown to be an effective way to observe uranium sorption in existing wells. The analysis of samplers that have been processed during this internship has concluded sorption of uranium varies for sediment of different initial concentrations of sorbed humate. In FAW-5, higher concentrations of humate, at 300 ppm, lead to a decrease in aqueous uranium concentrations and an increase in sorption to sediment, determined by the uranium distribution coefficient. It was also determined that humate remained sorbed onto sediment after the 5 months in the well, indicating the longevity of humate. A possible future diffusion sampler study could include deploying samplers for a longer period of time to observe the lasting effectiveness of humate. The remaining work left for this experiment includes analyzing groundwater samples for I-129 and sediment for TOC. This study contributes to the Attenuation-Based Remedies for the Subsurface Applied Field Research Initiative, as well as the research supporting the humate field injection test SRNL performed in 2013.

6. REFERENCES

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