Investigation of the Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems

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EXECUTIVE SUMMARY

Flow-through column experiments were conducted at the Florida International University (FIU) Applied Research Center (ARC) to estimate the sorption and desorption properties of humic acid onto Savannah River Site (SRS) sediment and to study the mobility of uranium through humic acid sorbed sediment. Previous studies have shown that humic acid sorbed to sediments will strongly bind with sediments at a mildly acidic pH. The use of humic acid could be applied to various DOE sites for contaminant stabilization; however, column studies are required to optimize this technology and prepare it for actual field deployment and regulatory acceptance. Experiments were designed to study the behavior of humic acid, specifically Huma-K, at different pH levels to help develop a model to predict the humic acid sorption/desorption.

This report provides the background information, methodology, and results from tracer tests and humate injection tests in flow-through columns filled with sediment from SRS followed by uranium injection through humate sorbed sediment. Tracer test provided transport parameter values and showed that the column has high dispersion. The humate breakthrough curve spread is higher than that of the bromide tracer due to precipitation and re-dissolution of humic acid. Approximately 670 - 738 mg of humic acid was retained per kg of sediment. Additionally, 51.95 µg of uranium was sorbed on the sediment per kg. Further experiments will include additional tests to include different pH levels.

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LIST OF ACRONYMS

AGW	Artificial groundwater
ARC	Applied Research Center
DIW	Deionized water
DOE	U.S. Department of Energy
FIU	Florida International University
HA	Humic acid
HS	Humic substances
HWMF	Hazardous Waste Management Facility
PV	Pore volume
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

Introduction

The Savannah River Site (SRS) was established as one of the major U.S. Department of Energy (DOE) facilities for the production of materials related to the U.S. nuclear program during the early 1950s. The F-Area Hazardous Waste Management Facility (HWMF) consists of three unlined, earthen surface impoundments, referred to as seepage basins. From 1955 to 1988, the F-Area seepage basins received approximately 1.8 billion gallons of low level waste solutions generated by uranium slug and irradiated fuel processing in the F-Area Separations Facility. The effluents were acidic due to the presence of nitric acid and a contained a wide variety of radionuclides and dissolved metals (Dong et al., 2012). The waste solutions were moved approximately 3,000 feet from each processing area through underground clay pipes to the basins. Once the wastewater entered the basin, it was allowed to evaporate and seep into the underlying soil. The basins were intended to minimize contaminant migration to exposure points through the interactions with the basin soils. Although they performed as designed, due to the acidic nature of the basin influent, there was mobilization of some metals and radionuclides of uranium isotopes, ¹²⁹I, ⁹⁹Tc, and tritium, which migrated into the groundwater to create an acidic plume with a pH between 3 and 5.5.

Beginning in the late 1950s, the groundwater at the basins has been monitored and assessed. Remediation efforts and assessments have been applied through the years using various types and numbers of wells, seepline monitoring points and surface water locations. Although the site has gone through years of active remediation, the groundwater remains acidic, with pH as low as 3.2 around the basins and increasing to pH 5 down gradient. In addition, U(VI) and other radionuclide concentrations remain above their maximum contaminant levels. In an effort to remove the contaminants from the groundwater, pump-and-treat and re-inject systems were implemented in 1997. Down gradient contaminated groundwater was pumped to a water treatment facility, treated to remove metals (through osmosis, precipitation/flocculation, and ion exchange), and then re-injected upgradient within the aquifer. The pump-and-treat water treatment unit eventually became less effective, generated large amounts of radioactive waste and was expensive to maintain, prompting research for new remedial alternatives. In 2004, the pump-and treat system was replaced by a funnel and gate system in order to create a treatment zone via injection of a solution mixture

composed of two components, sodium hydroxide and carbonate. The injections were done directly into the gates of the F-Area groundwater to raise pH levels. The purpose of the treatment zone was to reverse the acidic nature of the contaminated sediments, thereby producing a more negative net charge on the surface of sediment particles and enhancing adsorption of cationic contaminants. This system of remediation required a systematic re-injection of the base to raise the pH to near neutral values. However, the continuous use of high concentrations of a carbonate solution to raise pH creates a concern of possible re-mobilization of uranium that was previously adsorbed within the treatment zone since U(VI) in the presence of bicarbonate ions forms soluble aqueous uranyl-carbonate complexes.

Savannah River National Laboratory (SRNL) has been testing an unrefined, low cost humic substance known as Huma-K as an amendment that can be injected into contaminant plumes to enhance sorption of uranium, Sr-90, and I-129. A field test of the humic acid technology for uranium and iodine-129 (I-129) was conducted by Millings et al. (2013) at the F-Area Field Research Site. Humic substances are ubiquitous in the environment, occurring in all soils, waters, and sediments of the ecosphere. Humic substances are complex heterogeneous mixtures of polydispersed materials formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains. Humic substances (HS) account for 50-80% of the organic carbon in the soil or sediment and are known for their excellent binding capacity for metals, while being insoluble or partially soluble. This makes HS a strong candidate for remediation efforts to reduce the mobility of uranium (VI) in the subsurface. Three main fractions of HS are identified based on their solubility in dilute acids and bases. Their size, molecular weight, elemental composition, structure, and the number and position of functional groups vary.

Humic acids: the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values. They can be extracted from soil by various reagents, which are insoluble in dilute acid. Humic acids are the major extractable component of soil humic substances. They are dark brown to black in color.

Fulvic acids: the fraction of humic substances that is soluble in water under all pH conditions. They remain in solution after removal of humic acid by acidification. Fulvic acids are light yellow to yellow-brown in color.

Humin: the fraction of humic substances that is not soluble in water at any pH value and in alkali. Humins are black in color.

The Huma-K commercially available dry flake organic amendment was used as a source of humic acid for these experiments. Huma-K is high in humic and fulvic compounds and is just one of several brands produced for large scale use as soil conditioners to boost productivity in organic agriculture and used by farmers to stimulate plant growth and facilitate nutrient uptake. Huma-K is made from leonardite, an organic rich mineral formed due to decomposition by microorganisms, by extracting the raw material with a potassium hydroxide base solution and then drying it. The high pH solubilizes the humic acid molecules and generates a dark-brown highly-concentrated solution, rich in humic acid, which can be diluted for use. Importantly, while such solutions are commonly called soluble humic acid, they are actually basic with pH greater than 7.

Methodology

Sediment Characterization

Sediment previously obtained from SRS and characterized during characterized by FIU during 2014 was used in the experiments. The sediment sample was obtained from SRS's FAW-1 at a depth of 60'-70'. Sediment was disaggregated with minimal force to avoid creating new mineral surfaces due to fracturing and abrasion using a 2-mm sieve to collect sediment of particle size ≤ 2 mm.

Column Experiments

Glass column (25 mm x 300 mm) obtained from Ace Glass Inc. was used to conduct the flowthrough column experiment to study the sorption/desorption of humic acid onto SRS sediment and to study the mobility of uranium through humic acid sorbed sediment. Column fitted with Teflon® adapters containing 350 micron screen support and a layer of glass wool (Figure 1) was filled with a known mass of oven dried sediment obtained from SRS (Figure 2).



Figure 1. Teflon ® adapter with layer of glass wool.



Figure 2. Column with SRS sediment before and after saturation with DIW.

Column Tracer Test

A bromide tracer test was performed to obtain transport parameters; prior to performing the tracer tests, the columns were saturated with deionized water (DIW) from the bottom of the column to the top in order to remove air bubbles. Flow of DIW was continued until the effluent flow rate of 2 ml/min was achieved. After flow was equilibrated, 4 ml of a 1000 ppm bromide solution was injected at the top of the column. Samples of effluent were collected in pre-weighed containers at regular intervals. After each interval, the containers with samples were re-weighed and the bromide concentration was measured using a Thermo Scientific Orion Bromide Electrode (9635BNWP). Samples were collected until the bromide effluent readings reached equilibrium. Data collected allow for the determination of mean residence time, as well as the pore volume of the column. Prior to measuring the bromide concentration using a bromide electrode, the electrode was calibrated using bromide standards in the range of 0.5 - 100 ppm (Figure 3).



Figure 3. Calibration curve for bromide electrode.

The residence distribution function, E(v), as a function of volume fractions (Levenspiel, 1972) was calculated using Eq. 1:

$$E(v) = \frac{C(v)}{\int_0^\infty C(v) \, dv}$$
 Eq. (1)

Where:

v - Volume of effluent

C(v) - Concentration of bromide

Mean residence time (t_m), and pore volume (V_p) (Shook et al., 2005) were estimated using Eq. 2 and Eq. 3:

$$t_m = \frac{\int_0^\infty t E(t) dt}{\int_0^\infty E(t) dt} = \int_0^\infty t E(t) dt \qquad \text{Eq. (2)}$$

$$V_p = \frac{\int_0^\infty v E(v) dv}{\int_0^\infty E(v) dv} = \int_0^\infty v E(v) dv \qquad \text{Eq. (3)}$$

Where:

t - Time

E(t) - Residence distribution function in terms of time

v - Volume of effluent

E(v) - Residence distribution function in terms of volume

Variance and the dimensionless Peclet number (P_e), which represents the ratio of the rate of transport by convection to the rate of transport by diffusion or dispersion, were determined by solving the 1D dispersion/advection equation (Bischoff et al., 1963; Fogler et al., 1992; Mibus et al., 2007):

Variance
$$(\sigma^2) = \int_0^\infty (v - v_p)^2 E(v) dv$$
 Eq. (4)

$$\frac{\sigma^2}{t_m^2} = \frac{2}{P_e^2} \left(P_e - 1 + e^{-P_e} \right)$$
 Eq. (5)

Where:

v - Volume of effluent

v_p - Pore volume

E(v) - Residence distribution function in terms of volume

Sorption/Desorption of Huma-K

After the tracer test, the column was preconditioned using pH adjusted artificial groundwater (AGW). Artificial groundwater that mimics SRS groundwater characteristics was prepared according to Storm and Kabak (Storm & Kaback, 1992) by dissolving 5.4771 g CaCl2, 1.0727 Na2SO4, 3.0943 g MgCl2, 0.3997 KCl, and 2.6528 NaCl in 1 L of deionized water (Barnstead NANOpure water purification system). 0.84995 g NaNO₃ was dissolved to obtain a 0.01M NaNO₃ solution. One (1) mL of the stock solution was diluted into 1 L of deionized water acidified to the desired pH to create a working solution. AGW pH adjusted to 3.5 was pumped from the bottom of the column until the pH of the effluent solution reached equilibrium (at pH 3.55). Once the pH of the effluent reached equilibrium, approximately one pore volume (PV) of 10,000 ppm Huma-K

solution, pH adjusted to 9 using 0.1 M HNO₃, was pumped at the same flow rate (2 ml/min) used during the tracer test. After injecting 1 PV of the Huma-K solution, pH 3.5 adjusted AGW solution was pumped into the column until the effluent concentration reached approximately 2% of the initial concentration; effluent samples were collected to measure the change in pH and concentration of Huma-K. The concentration of Huma-K in the effluent was measured immediately after collecting the sample to ensure the desired end point of the desorption phase was achieved. Samples were analyzed using a Thermo Scientific Genesys 10S UV-Vis spectrophotometer; calibration of the UV-Vis was performed using standards in the range of 1 to 25 ppm and at wavelength of 254 nm (Figure 4). Also, the E4/E6 ratio (ratio between the absorbance at 465 nm and 665 nm) and the E_{Et}/E_{Bz} ratio (ratio of absorbance at 253 nm and 220 nm) was measured using the UV-Vis spectrophotometer.

Sorption/Desorption of Uranium

After sorption and desorption of Huma-K, 2 PV of 100 ppb uranium prepared with AGW at pH 3.5 was injected through the column with Huma-K sorbed sediment to study the mobility of uranium. The desorption of uranium was studied by injecting 2 PV of 3.5, 4.5 and 5.5 pH adjusted AGW solutions, respectively.



Figure 4. Humic acid calibration curve.

Results and Discussion

Bromide Tracer Tests

Column was filled with 256.31 g of oven-dried SRS sediment that was sieved through a 2-mm sieve. After the column was filled and saturated with DI water, a bromide tracer test was performed by following the procedure detailed in the methodology section. The data obtained from the tracer test is presented in Figure 5 and Table 1. Figure 5 shows the change in concentration of bromide versus the volume of collected effluent fractions. The pore volume, variance and Peclet number were calculated using equations 1-5 as described in the methodology section and the data is presented in Table 1 and Table 2. The results show that the column has a pore volume of 87.72 ml and a greater variance value positively correlates with a greater distribution spread.



Figure 5. Co	oncentration	of measured	bromide.
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Table 1. Tracer Test Results										
Sediment weight (g)	Flow rate (ml/min)	Bromide added (mg)	Recovery (%)	Total fluid collected (mL)	Pore volume (ml)					
256.31	2.0	4.0	3.72	93	371.85	87.72				

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The dimensionless Peclet number (Pe) is defined as the ratio of the rate of transport by convection to the rate of transport by diffusion or dispersion (Eq. 6). Pe, found experimentally from the tracer test, was used to calculate effective dispersion (Table 2); the values of the Peclet number were used to correlate the effect of dispersion on the effluent tracer concentration.

$$Pe = \frac{\text{rate of transport by convection}}{\text{rate of transport by diffusion or dispersion}} = \frac{UL}{D_a}$$
Eq. (6)

Where:

L - characteristic length term (m)

 D_a - effective dispersion coefficient (m²/s)

U - average interstitial velocity (m/s)

Table 2. Transport Parameters Determined by Bromide Tracer Injection

U (m/s)	Variance, σ ²	Pe	Dispersion (m²/s)	1/Pe=D/uL	Dispersion
$4.09 imes 10^{-4}$	263.9	14.0	$8.76 imes 10^{-6}$	0.071	High

Sorption and Desorption of Humic Acid

Following the bromide tracer test, AGW with pH adjusted to 3.5 was pumped from the bottom of the column until the pH of the effluent solution reached equilibrium (at pH 3.55). One (1) PV of 10,000 ppm of Huma-K with pH adjusted to 9 was then pumped at a flow rate of 2 ml/min. The humic solution was stirred continuously while pumping to avoid settling. After injecting approximately 1 PV of the humic solution, AGW at pH 3.5 was injected into the column until the concentration of Huma-K reached approximately 2% of the initial concentration while collecting effluent samples at 4 minute intervals. The concentration of humic acid in the effluent samples was measured immediately after sample collection in order to ensure that the desired end point of the desorption phase was achieved. It was observed that approximately 2.2 PV of AGW with pH adjusted to 3.5 was required to reach 2% of the initial humic acid concentration. The effluent sample pH was also measured and recorded.

Figure 6 shows the breakthrough curve of humic acid sorption and desorption in the column and the change in pH. It is evident from the curve that most of the humic acid injected into the column was retained in the column and no humic acid was observed in the effluent solution until after 0.75

pore volumes. After 0.75 pore volumes, the concentration of humic acid increased and reached a peak value of approximately 5,700 ppm while the pH started to rise. When HA at pH 9 was injected into the pH 3.5 column, precipitation and re-dissolution of HA might have occurred as the pH of the solution increased; this would explain the spread of the breakthrough curve compared to that of the non-reactive bromide breakthrough curve. Because of precipitation, the amount of HA sorbed is inconclusive and the term "retained" is used over "sorbed" in this report. Around 2 PV, the concentration of HA started to decrease and the concentration of humic acid in the effluent reached 197 ppm after injecting approximately 2.2 PV of AGW at pH 3.5. Table 3 shows the results obtained from sorption and desorption of Huma-K; the pH of the column changed from 3.55 to 8.79 while retaining approximately 189 mg of humic acid out of 829 mg of humic acid, resulting in a retention total of 738 mg of humic acid per kg of sediment.



Figure 6. Concentration profile of HA in the effluent of the column.

Sediment	pl	H	Humic acid				
weight (g)	Initial	Final	Volume injected (ml) Injected (mg)		Recovered (mg)	Retained (mg/kg)	
256.31	3.55	8.79	82.9	829.00	639.77	738.29	

Table 3. Soprtion/Desorption of Humic Acid

Since the humic acid solution was prepared from unrefined Huma-K, the humic solution was composed of humic acid and fulvic acid of different sizes and molecular weights; the E_4/E_6 ratio was used to determine which humic fraction sorbed onto the sediments. The E_4/E_6 ratio was calculated by dividing the absorbance of the sample at 465 nm by 665 nm. Researchers have found that the E_4/E_6 ratio increases as the average molecular weight of humic substances decreases. The range of values of the E_4/E_6 ratio from a wide variety of literature sources for humic acids and fulvic acids are 3.8-5.8 and 7.6-11.5, respectively; however, the E_4/E_6 ratios obtained during the experiment were in the range of 1.0 - 7.0. Where the concentration of humic acid in the effluent was high, the experimental E_4/E_6 ratios were in the range of 3.5 - 7.0, meaning that the fraction of humate bound to the sediments consists of humic acid molecules.

The E_{ET}/E_{BZ} ratio was calculated in order to determine the degree and possible nature of substitution. The ratio was calculated by measuring the absorbance at 253 nm and 220 nm, corresponding to the electron-transfer band and the benzenoid band, respectively. The intensity of the absorbance, especially the electron-transfer band, has a significant increase when substitution increases. The benzene band is almost unaffected. A low E_{ET}/E_{BZ} ratio indicates scarce substitution in the aromatic rings or substitution with aliphatic functional groups, while a high E_{ET}/E_{BZ} ratio indicates the presence of O-containing functional groups (hydroxyl, carbonyl, carboxyl, and ester groups) on the aromatic ring. The ratios vary from 0.03 (benzene ring), to between 0.25-0.35 for phenolic compounds and above 0.40 for aromatic rings with carbonyl and carboxylic groups. The values of the E_{ET}/E_{BZ} ratios were observed to be around 0.8 - 0.9, indicating that the aromatic structures in these humic molecules probably have a higher degree of substitution with oxygen-containing functional groups.

Sorption and Desorption of Uranium

Sorption and desorption of uranium in the humate sorbed column was studied by injecting 2 PV of a 100 ppb uranium solution prepared with SRS AGW at pH 3.5 followed by injection of 2 PV of AGW at pH 3.5, 4.5 and 5.5, respectively. Figure 7 shows the change in the concentration of uranium and change in pH while injecting the uranium solution through the column. The pH of the column decreased from 8.8 to 7.79 while 100 ppb of uranium at pH 3.5 was injected into the column.



Figure 7. Change in uranium concetration and pH during uranium injection.

Figure 8 and Figure 9 show the change in humic acid concentration during injection of uranium and AGW solution at pH 3.5, respectively. Approximately 15 mg of humic acid was recovered from the effluent solution during the uranium injection, and total of 2.4 mg of humic acid was recovered during injection of the AGW solution with pH 3.5; no humic acid was recovered during injection of pH 4.5 and 5.5 AGW.

sediment	pH		Humic acid					
weight (g)	Initial	Final	Volume injected (ml)	Injected (mg)	Recovered (mg)	Retained (mg/kg)	Total Recovered (mg)	Total Retained (mg/kg)
256.31	3.55	8.79	82.9	829.00	639.77	738.29	657.44	669.33

Table 4. Soprtion/Desorption of Humic Acid after Uranium Injection



Figure 8. Change in Huma-K concentration during uranium injection.



Figure 9. Humic acid recovery after uranium injection.

Figure 10 shows the change in uranium concentration and pH in the effluent solution during injection of the uranium solution and AGW (pH adjusted to 3.5 - 5.5). Approximately 16.4 µg of uranium was injected into the column; the amount of uranium recovered during the uranium injection and AGW at pH 3.5 were 2.43 µg and 0.568 µg, respectively. The concentration of uranium in the effluent solution during the injection of pH 4.5 and 5.5 AGW was below the detection limit of KPA. Samples collected during this phase of experiments were spiked with a known amount of 100 ppb uranium solution and reprocessed to obtain the concentration of uranium in the samples. The amounts of uranium recovered at this stage of the experiment were 0.026 µg and 0.03 µg, respectively. Table 5 shows the results obtained from sorption and desorption of uranium; overall, approximately 52 µg/kg of uranium was sorbed on to Huma-K sorbed sediment.



Figure 10. Change in uranium concentraion during sorption and desoprtion of uranium.

Sediment	pl	H	Humi	c acid		Uranium	
weight (g)	Initial	Final	Retained (mg)	Retained (mg/kg)	Injected (µg)	Recovered (µg)	Retained (µg/kg)
256.31	8.79	4.43	171.56	738.29	16.39	3.05	51.95

Table 5. Soprtion/Desorption of Uranium

Future Work

FIU will continue to perform the humic acid sorption/desorption experiments at varying pH levels and varying humic acid concentrations to study uranium mobility though the humate sorbed columns.

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References

- 1. Bear, Jacob, Hydraulics of Groundwater, McGraw-Hill Book Company, New York 1979.
- 2. Bischoff K., Levenspiel O., (1963) Adv. Chem. Eng. 4, p. 95.
- 3. Blake, G.R., and Hartge, K.H., (1986). Bulk Density. In: Klute, A. (Ed.), Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. American Society of Agronomy-Soil Science Society of America, 677 South Segoe Road, Madison, WI, 363-375.
- 4. Blake, G.R., and Hartge, K.H., (1986). Particle Density. In: Klute, A. (Ed.), Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. American Society of Agronomy-Soil Science Society of America, 677 South Segoe Road, Madison, WI, 377-382.
- Danielson, R.E., and Sutherland, P.L., (1986). Porosity. In: Klute, A. (Ed.), Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. American Society of Agronomy-Soil Science Society of America, Madison, WI, 443-450.
- Dong, W., Tokuanga, T. K., Davis, J. A., Wan, J., (2012). Uranium(VI) Adsorption and Surface Complexation Modeling onto Background Sediments from the F-Area Savannah River Site. Environ. Sci. Technol. 46, 1565-1571.
- 7. Fogler, H., S., (1992). Elements of Chemical Reaction Engineering, PTR Prentice-Hall, Inc., 837p.
- 8. Levenspiel, O., Chemical Reaction Engineering, 2nd Ed., (1972), John Wiley & Sons.
- 9. Mibus, J., Sachs, S., Pfingsten, W., Nebelung, C., Bernhard, G., (2007). Migration of Uranium (IV)/(VI) in the Presence of Humic Acids in Quartz Sand: a Laboratory Column Study, Journal of Contaminant Hydrology, Volume 89, Issues 3-4, Pages 199-217.

- 10. Milling, M. R., Amidon, M. B., Denham M. E., Looney B. B., (2013). Preliminary Data Report: Humate Injection as an Enhanced Attenuation Method at the F-Area Seepage Basins, Savannah River Site (U). (SRNL-STI-2013-00514).
- 11. Ptak, T., Piepenbrink, M., Martac E. (2004). Tracer Tests for the Investigation of Heterogeneous Porous Media and Stochastic Modelling of Flow and Transport a Review of some Recent Developments, Journal of Hydrology, 122 163.
- 12. Shook, G. M., Forsmann, J. H., (2005). Tracer Interpretation Using Temporal Moments on a Spreadsheet (INL/EXT-05-00400).
- 13. Storm, R.N., Kaback, D.S. 1992. SRP Baseline Hydrogeologic Investigation: Aquifer Characterization, Groundwater Geochemistry of the Savannah River Site and Vicinity (U). Westinghouse Savannah River Company, Savannah River Laboratory.
- 14. Wan, J., Dong, Wenming, and Tokunaga T. K., (2011) Method to Attenuate U(VI) Mobility in Acidic Waste Plumes Using Humic Acids, Environ. Sci. Technol. 2011, 45, 2331–2337
- 15. Wan, J., Tokuanga, T. K., Dong, W., Denham M. E., Hubbard, S. E., (2012). Persistent Source Influences on the Trailing Edge of a Groundwater Plume, and Natural Attenuation Timeframes: The F-Area Savannah River Site. Environ. Sci. Technol. 46, 4490-4497.