Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems – 16523

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ABSTRACT

The Savannah River Site (SRS) was one of the major U.S. Department of Energy facilities that produced large amounts of radioactive and hazardous waste during the Cold War era, a legacy of material production for defense purposes. The unlined F-Area seepage basins received approximately 1.8 billion gallons of acidic waste solutions containing low-level radioactivity from numerous isotopes generated by uranium slug and irradiated fuel processing. Sufficient quantities of uranium isotopes, I-129, Tc-99, and tritium migrated into the groundwater, creating an acidic plume with a pH between 3 and 5.5.

Humic substances (HS) are complex heterogeneous mixtures of polydispersed materials formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains. They are known for their excellent binding capacity for metals, making them a strong candidate for remediation efforts to reduce the mobility of uranium (VI) in the subsurface. Studies showed that HS are an important ion exchange and metal-complexing ligand, carrying a large number of functional groups with high complexing capacity that can greatly affect the mobility behavior of actinides in natural systems. Hence, it is a potential in situ amendment for treating groundwater contaminated with these constituents.

Column experiments were conducted to address the complexities of HS in flow-through porous media representative of the acidic aquifer at the SRS F-Area Seepage Basins. The humate source used, Huma-K, is high in humic and fulvic compounds. The column studies were done using the soil obtained from SRS's FAW-1 corehole at a depth interval of 60'-70'. A bromide tracer test was performed to obtain the pore volume (PV), variance and Peclet number. The columns were saturated with an artificial groundwater solution prepared to mimic the groundwater at SRS that was pH adjusted to 3.5 and 5 until the effluent pH reached equilibrium. Approximately one (1) PV of 5000 ppm of Huma-K was injected into the columns at 2 ml/min to study the sorption of Huma-K on the sediment. Desorption of Huma-K was studied by injecting approximately four (4) PVs of the pH adjusted artificial groundwater solution. A faster increase in pH was observed in column 1 (saturated with pH 3.5 AGW) compared to column 2 (saturated with pH 5 AGW). After injection of 2 PV of AGW, the pH of the columns reached 6.5 and 7, respectively, for columns 1 and 2. After injecting an additional PV of AGW, the pH remained relatively stable. With an increase in pH from 3.5 to 5.0, the overall retention of HA increased from 461 mg/kg for the column with pH 3.5 to 642 mg/kg for the column with pH 5. This suggests that retention is not due to adsorption alone, but adsorption coupled with precipitation and re-dissolution of Huma-K as it flows through the columns is a possible explanation for greater retention at pH 5. This negates the use of a simple Langmuir isotherm to explain humate behavior in the acidic environment of column 1.

INTRODUCTION

The Savannah River Site (SRS) was one of the major U.S. Department of Energy (DOE) facilities that produced plutonium during the Cold War. 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 wide variety of radionuclides and dissolved metals [8]. 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, there was mobilization of some metals and radionuclides, in particular uranium isotopes, I-129, Sr-90, Tc-99, and tritium that migrated into the groundwater to create an acidic plume with a pH between 3 and 5.5.
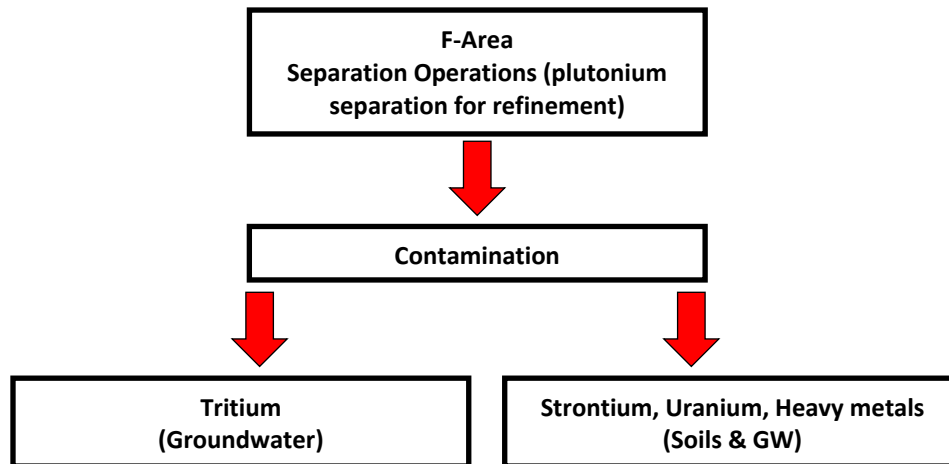

Figure 1. Source of contamination and contaminants.

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 of 5 down gradient. In addition, U(VI) and other radionuclide concentrations remain above their maximum contaminant levels in parts of the aquifer. 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 up 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 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 and possibly I-129. This was prompted by the study by Wan et al. of a more refined humic acid to enhance attenuation of uranium in the acidic F-Area aquifer [19]. A field test of humic acid technology for uranium and I-129 was conducted by Millings et al. [13] 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. The high affinity for aqueous metals allows the fate of the metals to be controlled by the behavior of humic substances [14]. 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. 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. Factors that influence the transport of humate in porous media are mechanical, such as molecular shape, concentration, and flow rate, as well as physicochemical factors, like pH and porous media surfaces [21]. In this study, humate solution was introduced to a porous soil system, saturated with artificial groundwater at different pH, and observed to understand the effects in transport of humate. The method used to determine the transport parameters was through column experiments.

METHODS
Soil Characterization

Soil obtained from SRS's FAW-1 core hole at the 60'-70' depth interval was characterized to determine the physical properties and pH of the soil. Soil was disaggregated with minimal force to break large chunks and was sieved using a 2 mm sieve to collect sediment of a particle size ≤2 mm.

Bulk Density Analysis

The dry bulk density of a solid is defined as the ratio of the dry mass of solids to its bulk volume (solid and void volume). The volume of the soil was measured without compaction and the mass of the soil was determined after drying a known volume in the laboratory oven [4]. The bulk weight of the soil amendment mixtures was determined gravimetrically. Triplicate samples in 50-mL beakers were used and filled with soil, while the volume was noted. The soil was dried at 105°C for one day to stabilize weight and its mass was determined after cooling in a desiccator. The

$$\text{Bulk density} = \frac{\text{Oven dried soil weight}}{\text{Volume of soil}}$$

bulk density of the soil was calculated using

(Eq. *1*):

$$\text{Bulk density} = \frac{\text{Oven dried soil weight}}{\text{Volume of soil}} \qquad \text{(Eq. 1)}$$

Particle Density Analysis

The particle density of a solid is defined as the ratio of the mass of solids to the volume of solids. The Methods of Soil Analysis for the Pycnometer Method was used to determine the particle density of the soil [5]. Using triplicate samples, 12.5 g of soil were air dried, weighed and introduced to an oven dried and pre-weighed 25-mL volumetric flask. Deionized water (DIW) was added to fill the flasks to the half-way point and gently boiled for a few minutes to eliminate air bubbles. After cooling, the flasks were filled to the 25 mL mark from previously boiled and cooled DIW. The particle density was determined for the soil using **Error! Reference source not found.**:

$$\rho_p = \frac{\rho_w (W_s - W_a)}{[(W_s - W_a) - (W_{sw} - W_w)]} \qquad \text{(Eq. 2)}$$

Where:

ρ_w - Density of water in grams per cubic centimeter at observed temperature
W_s - Weight of volumetric flask plus soil
W_a - Weight of empty flask
W_{sw} - Weight of flask filled with soil and water slurry
W_w - Weight of flask filled with water at observed temperature

The porosity of the soil was determined using the calculated bulk and particle density, and is defined as the ratio of void volume of the soil to its total volume. Total porosity of the samples was calculated using the following formula [7]:

$$n = 1 - \frac{\rho_b}{\rho_p}$$
(Eq. 3)

The pH of the soil sample was also estimated using a 1:1 soil:water suspension ratio. In triplicate beakers, 10 g of soil and 10 mL of DIW were stirred for 15 minutes, and then settled for 15 minutes. The pH was measured using the supernatant of the soil samples.

Column Experiments
Glass columns (25 mm x 300 mm) obtained from Ace Glass Inc., were used to conduct flow-through column experiments to study the sorption and desorption characteristics of humic acid onto SRS sediment. Columns fitted with Teflon® adapters containing 350 micron screen support and a layer of glass wool were filled with a known mass of oven dried soil obtained from SRS.

Column Tracer Test
In this experiment, a bromide tracer was injected into the column and effluent concentrations were monitored. Prior to performing the tracer tests, columns were saturated with DIW from the bottom of the column to the top in order to remove air bubbles. Once air was removed from the column, the flow was reversed to move from top to bottom and left for flow to stabilize at the desired flow rate of 2 mL/min. After flow was equilibrated, 3 mL of 1000 ppm bromide solution was injected at the top of the column. Effluent samples 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 mean residence time to be determined, 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.

The residence distribution function, E(v) as a function of volume fractions [11] was

calculated using $$E(v) = \frac{C(v)}{\int_0^\infty C(v)\,dv}$$ (Eq. 4):

$$E(v) = \frac{C(v)}{\int_0^\infty C(v)\,dv}$$
(Eq. 4)

Where:

v - Volume of effluent
C(v) - Concentration of bromide

Mean residence time (tm), and pore volume (Vp) [16] were estimated using

$$t_m = \frac{\int_0^\infty t\,E(t)\,dt}{\int_0^\infty E(t)\,dt} = \int_0^\infty t\,E(t)\,dt$$

(Eq.   5)   and

$$V_p = \frac{\int_0^\infty v\,E(v)\,dv}{\int_0^\infty E(v)\,dv} = \int_0^\infty v\,E(v)\,dv$$

(Eq. 6):

$$t_m = \frac{\int_0^\infty t\,E(t)\,dt}{\int_0^\infty E(t)\,dt} = \int_0^\infty t\,E(t)\,dt$$

(Eq. 5)

$$V_p = \frac{\int_0^\infty v\,E(v)\,dv}{\int_0^\infty E(v)\,dv} = \int_0^\infty v\,E(v)\,dv$$

(Eq. 6)

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 (Pe), 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 [3; 9; 12]:

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

(Eq. 7)

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

(Eq. 8)

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) prepared using a 0.01 M NaNO3 solution mixed with 0.1 M HNO$_3$ or 0.1 M NaOH to reach the target pH values of 3.5 and 5. AGW was pumped from the top of the column until the pH of the effluent solution reached steady state. Once the pH of the effluent reached steady state, approximately one pore

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volume (PV) of 5000 ppm Huma-K solution, pH adjusted to 9 using 0.1 M HNO_3, was pumped at the same flow rate (2 mL/min) used during the tracer test. After injecting 1 PV of Huma-K solution, approximately 3 PV of AGW solution was pumped into the column and effluent samples were collected to measure the change in pH and concentration of Huma-K. Samples were analyzed using a Thermo Scientific Genesys 10S UV-Vis spectrophotometer calibrated in the range of 1 to 25 ppm of Huma-K at wavelength of 254 nm, to measure the concentration of HA.

A retardation factor can be used to describe the sorption capacity of soil. The retardation factor of humate in columns was estimated based on the mean residence time, tm, which can be expressed in terms of the aqueous volume, Vaq (Eq. 9). The final retardation factor is calculated using (Eq. *10)*, where Vp is pore volume determined from tracer tests.

$$V_{aq} = \frac{\int VC(t)dV}{\int C(t)dV} - \frac{V_{spike}}{2} \qquad \text{(Eq. 9)}$$

$$R = \frac{V_{aq}}{V_p} \qquad \text{(Eq. 10)}$$

The distribution coefficient of humate was calculated using the retardation factor and soil properties using (Eq. *11)* [2].

$$R = 1 + \rho_b \frac{K_d}{n} \qquad \text{(Eq. 11)}$$

RESULTS AND DISCUSSION
Soil Characterization
Soil obtained from SRS's FAW-1 at a depth of 60'-70' was used in the column experiments. The soil was first characterized to measure the bulk density, particle density, porosity and soil pH. Triplicate samples were prepared and analyzed using procedures described in the methods section and results of the average values obtained for each test are presented in Table I.

Table I. SRS Soil Characteristics

Bulk Density (g/cm^3)	Particle Density (g/cm^3)	Porosity	Soil pH
1.334	2.645	0.495	4.06

Humate Injection Scenarios
SRS developed a Langmuir model to simulate and observe breakthrough curves in humate injection scenarios. The model was used to estimate the flow rate and concentration of Huma-K to use in column experiments using the results obtained from soil characterization and previous batch experiments, along with the column size. Various concentrations and flow rates were applied to identify the optimum Huma-K concentration and flow rate; the concentrations applied in the simulations were in the range of 5,000 - 10,000 ppm at flow rates of 1 – 4 mL/min. At a high flow rate, the collision time of Huma-K with soil would decrease, reducing sorption in columns [5]. At a high concentration (10,000 ppm), the column is completely saturated (Figure 2) even at low flow rates; a lower concentration of 5,000 ppm of

Huma-K at 2 ml/min was found to be optimal for the size of the columns used in the experiments. The optimum scenario showed nice breakthrough curves with approximately 40% of Huma-K at 0.95 length of the column (Figure 3); whereas, a higher concentration of 10,000 ppm showed the column being saturated.

Bromide Tracer Tests

Two columns were filled with oven dried SRS soil that was sieved through a 2-mm sieve; the amount of soil used in each column was 257.511 g and 266.774 g, respectively. After the columns were filled with soil, a conservative bromide tracer test was performed by following the procedure detailed in the methods section. The data obtained from the column experiments is presented in Figure 4, Figure 5 and 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 (

$$Pe = \frac{rate\ of\ transport\ by\ convection}{rate\ of\ transport\ by\ diffusion\ or\ dispersion} = \frac{UL}{D_a}$$

(Eq. 12). Pe found experimentally from the tracer test was used to calculate effective dispersion (Table III); the values of the Peclet number were used to correlate the effect of dispersion on the effluent tracer concentration. The results from Table III show intermediate amounts of dispersion (1/Pe) in the range of 0.024 - 0.03.

$$Pe = \frac{rate\ of\ transport\ by\ convection}{rate\ of\ transport\ by\ diffusion\ or\ dispersion} = \frac{UL}{D_a}$$

(Eq. 12)

Where:
L - characteristic length term (m),
Da - effective dispersion coefficient (m2/s), and
U - average interstitial velocity (m/s).

. Figure 4 shows the change in concentration of bromide versus the volume of collected effluent fractions and Figure 5 shows the cumulative mass of bromide collected (bromide recovery) for both columns.
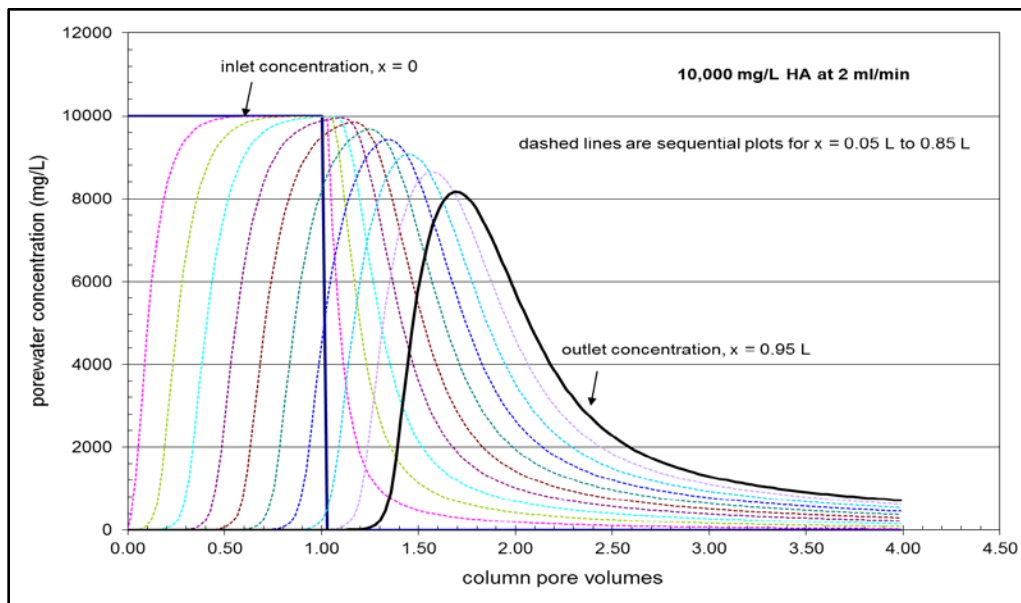

Figure 2. Huma-K injection scenario at 10,000 ppm at 2 mL/min.
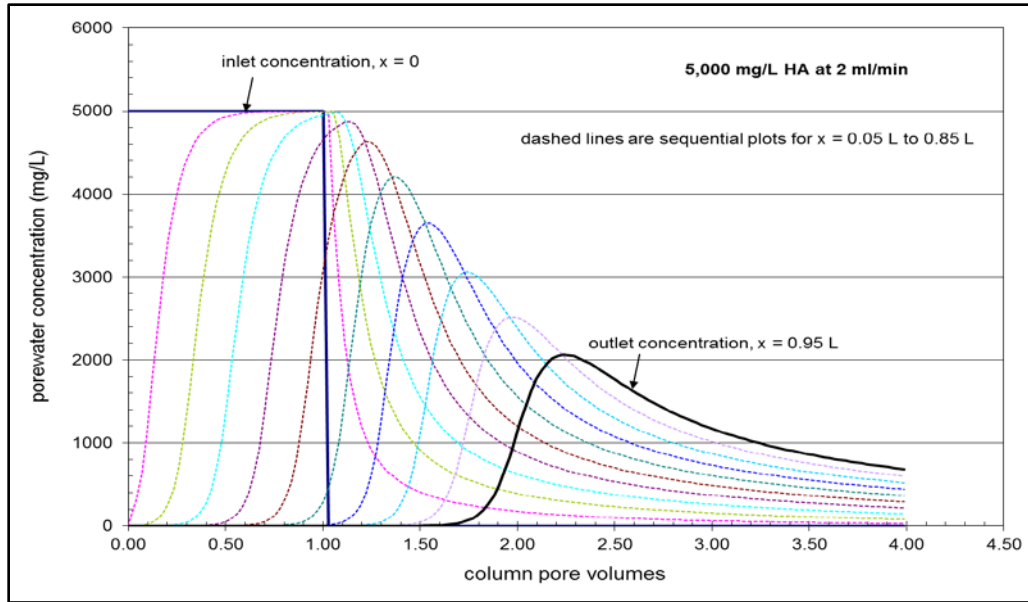
Figure 3. Huma-K injection scenario at 5,000 ppm at 2 mL/min.

Pore volume, variance and Peclet number were calculated using equations 4-8 as described in the methods section and the data is presented in 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 (

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(Eq. 12)

Where:
L - characteristic length term (m),
D_a - effective dispersion coefficient (m^2/s), and
U - average interstitial velocity (m/s).

and Table III. The variance indicates the spread of the distribution and a greater variance value positively correlates with a greater distribution spread. Column 1 has a pore volume of 85.8 mL, whereas column 2 has a pore volume of 74.12 mL; the difference could be due to the variance in soil compaction while filling the columns.
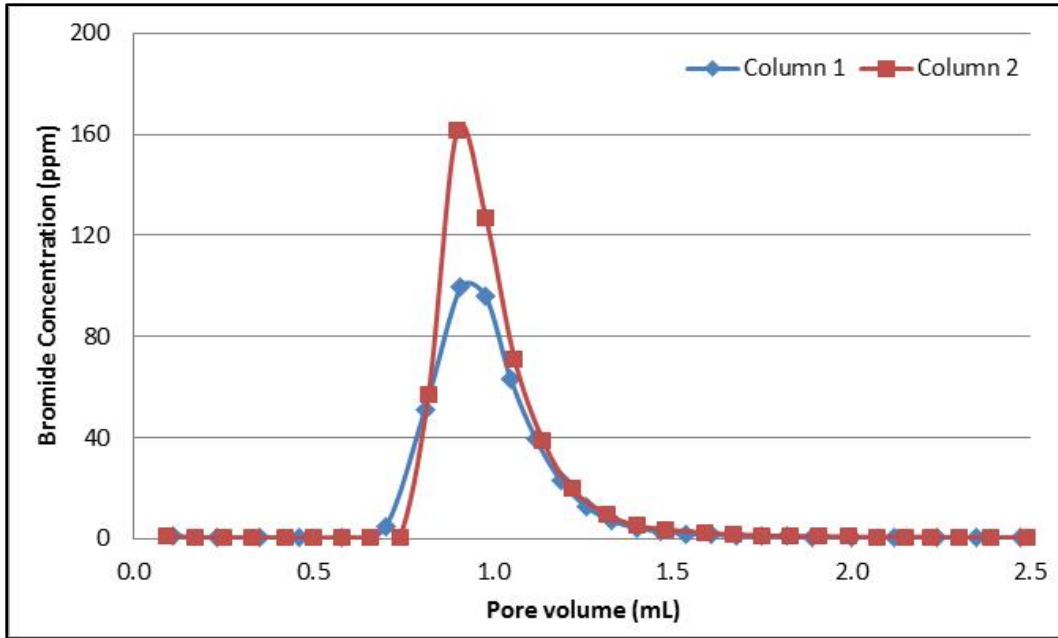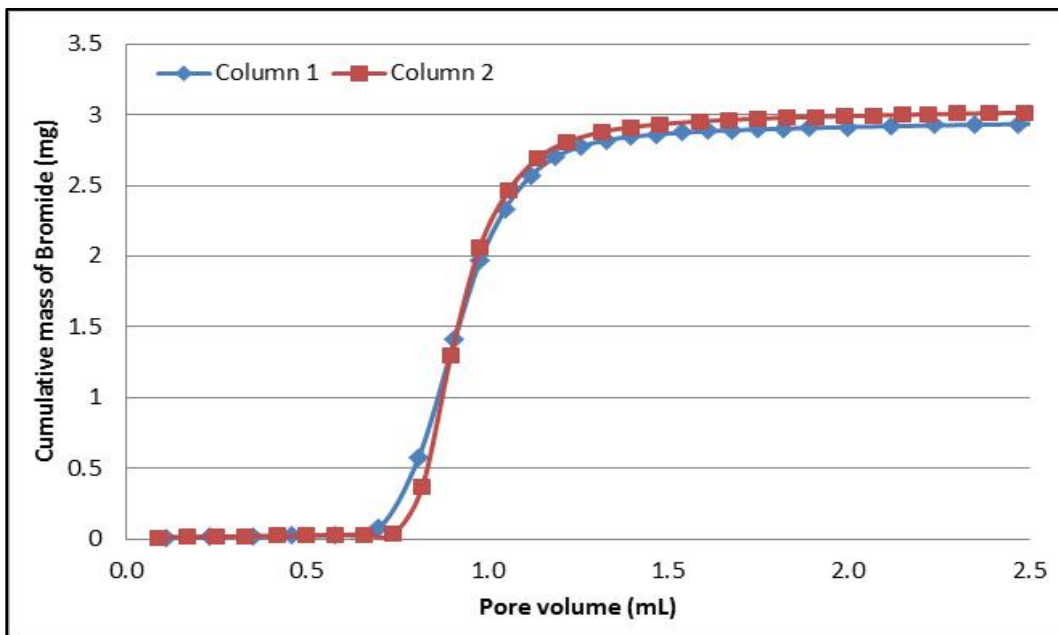
Figure 4. Concentration of measured bromide.

Figure 5. Cumulative mass of measured bromide.

Table II: Results of Tracer Tests

Column	Soil weight (g)	Flow rate (mL/min)	Bromide added (mg)	Bromide recovered (mg)	Recovery (%)	Total fluid collected (mL)	Pore volume (mL)
1	257.511	2.0	3.0	2.94768	98.2559	236.709	85.80
2	266.774	2.0	3.0	3.01533	100.511	180.998	74.12

Table III: Transport Parameters Determined by Bromide Tracer Injections

Column	U (m/s)	Variance, σ^2	Pe	Dispersion (m^2/s)	1/Pe=D/uL	Dispersion
1	4.09×10^{-4}	107.24	33.3	3.68×10^{-6}	0.03	Intermediate
2	4.09×10^{-4}	63.34	42.35	2.90×10^{-6}	0.024	Intermediate

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 ($Pe = \dfrac{rate\ of\ transport\ by\ convection}{rate\ of\ transport\ by\ diffusion\ or\ dispersion} = \dfrac{UL}{D_a}$ (Eq. 12). Pe found experimentally from the tracer test was used to calculate effective dispersion (Table III); the values of the Peclet number were used to correlate the effect of dispersion on the effluent tracer concentration. The results from Table III show intermediate amounts of dispersion (1/Pe) in the range of 0.024 - 0.03.

$$Pe = \frac{rate\ of\ transport\ by\ convection}{rate\ of\ transport\ by\ diffusion\ or\ dispersion} = \frac{UL}{D_a}$$ (Eq. 12)

Where:
L - characteristic length term (m),
D_a - effective dispersion coefficient (m^2/s), and
U - average interstitial velocity (m/s).

Sorption and Desorption Experiments

Following the bromide tracer test and preconditioning of the column, 1 PV of 5000 ppm of Huma-K with pH adjusted to 9 was 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, 4 PV of artificial groundwater solution with pH adjusted to 3.5 and 5.0 was injected into columns 1 and 2, respectively. Effluent samples were collected at regular intervals, the pH of the samples were measured, and the humic acid concentration was measured using a UV-Vis spectrophotometer.

The retardation factor was calculated to determine the ratio of the linear velocity of AGW to the velocity of humate. The retardation factors for columns 1 and 2 were 1.35 and 1.46, respectively. This can be compared to the recovery (R) from bromide tracer tests where the R values were approximately 1.0, as expected since bromide was used as a conservative tracer and moves at the same velocity of GW because there is no interaction with the soil. It was indicated that humate moved more slowly than the AGW, with it moving slower in column 2 with pH 5.0 than column 1 with pH 3.5. Sorption and precipitation effects are likely to be the primary causes of retardation; however, it was expected that at a lower pH, stronger sorption would occur, thus column 1 would have a greater R.

For column experiments, it must be assumed there is a relationship between the retardation factor and distribution coefficient, Kd [17]. The Kd was determined to quantify sorption reactions between humate and soil and defined as the ratio of the sorbed concentration per mass of solid to the aqueous concentration at equilibrium.

The distribution coefficients for columns 1 and 2 were determined to be 0.13 and 0.17 L/kg, respectively. This would indicate that the column with high pH had greater sorption than the column with lower pH, which was not expected. It is known that solutions will always flow through the more permeable path of media with the least resistance. These paths tend to decrease the time for reactions to occur, as well as the amount of soil surface exposed to flowing groundwater [1]. These effects prevent chemical equilibrium from being reached and should be considered when observing the Kd values. The tracer tests had determined column 1 had a greater pore volume and more dispersion than column 2, making it easier for humate to migrate through and for less sorption to occur. This may explain why the Kd value is lower for the low pH when it is expected to be higher.

Figure 6 shows the breakthrough curve of humic acid in the columns. It is evident from the curve that most of the humic acid injected into the column was initially retained in the column and no humic acid was observed in the effluent solution until after 1.5 pore volumes. After 1.5 pore volumes, the concentration of humic acid increased and reached a peak value of 6,000 ppm and 5,700 ppm for columns 1 and 2, respectively. Precipitation/re-dissolution of HA as it moves through the column is a possible explanation of the breakthrough curves formed. The high concentration of humate and steep pH gradient (humate at pH 9 to columns of pH 3.5 and 5) allows for chemical non-equilibrium to exist, and possibly causes precipitation/dissolution processes within the columns [17]. When HA was first injected into the columns, the amount of HA sorbed/deposited was great due to the rapid initial attachment of HA to soil. As more HA was injected, the binding sites at the mineral surfaces were quickly saturated due to the high HA concentration. With all the sites occupied, precipitation of HA may have also occurred sooner. As the high pH water was pushed through the zone of precipitation near the outlet, precipitated HA dissolved and thus the concentration at the outlet was higher than at the inlet concentration.
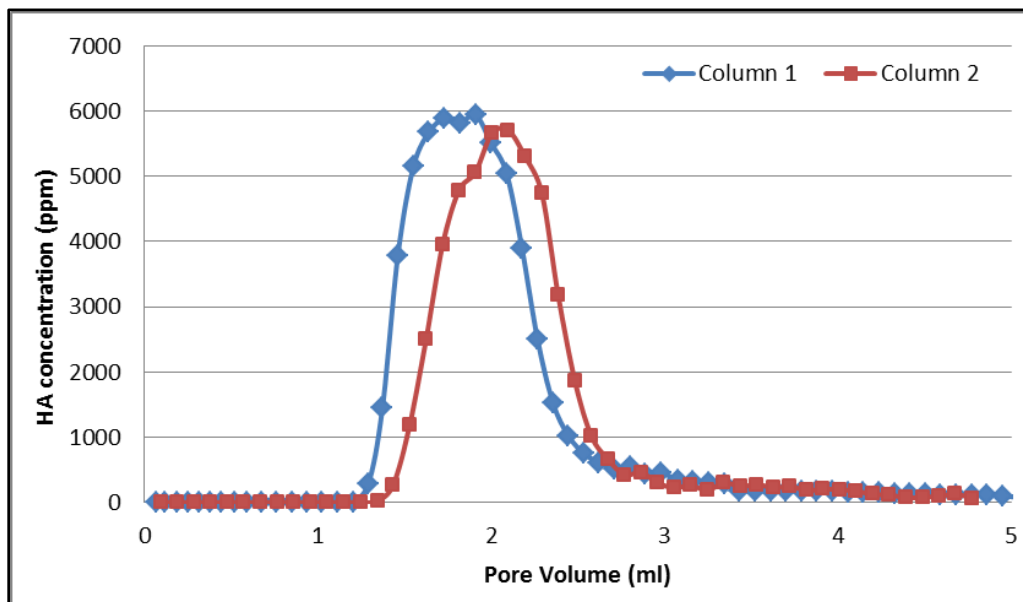

Figure 6. Concentration profile of HA in the effluent of the column.

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While HA moved down the column and the pH of the solution was increased, re-dissolution may have occurred, causing the spike in concentration for about 0.5 PV. After this, higher concentrations were no longer seen. This possibility also explains why the outlet concentration was greater than the inlet concentration. Around 2 PV, the concentration of HA started to decrease and then reached equilibrium. Because of precipitation, the amount of HA sorbed is inconclusive and the term "retained" is used over "sorbed".

Figure 7 shows the total mass of HA collected from the column; the amount of HA retained in the column was estimated by subtracting the amount of HA recovered from total HA injected (Table IV). Figure 8 shows the change in the amount of HA retained in the column with the pore volume of solution injected through the column.
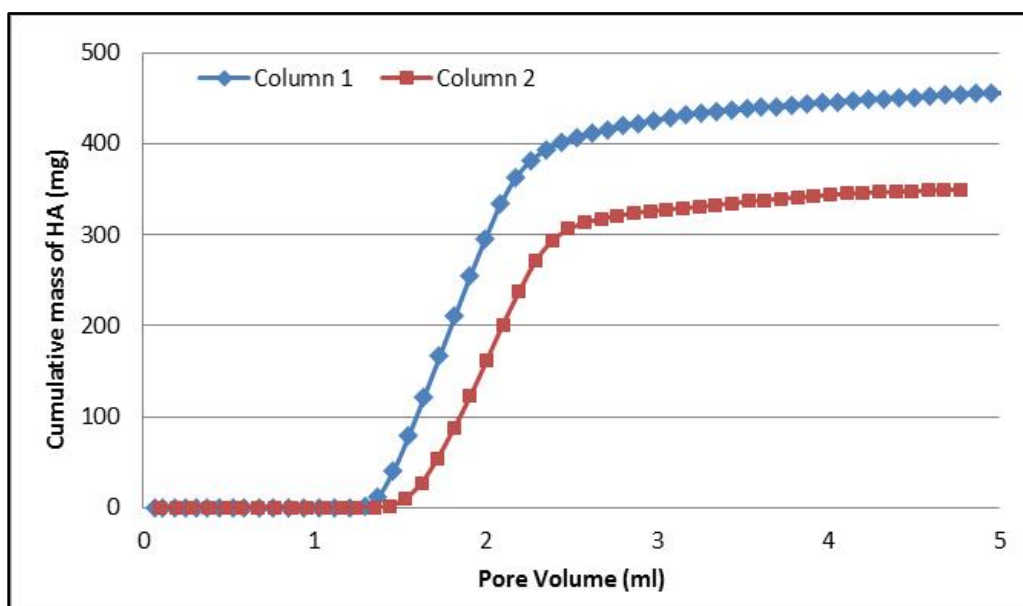

Figure 7. Cumulative mass of humic acid collected.

Table IV: Retention of Humic Acid

Column	Soil weight (g)	pH		Humic acid				
		Initial	Final	Volume injected (mL)	Injected (mg)	Recovered (mg)	Retained (mg)	Total Retained (mg/kg)
1	257.51	3.72	6.46	115.21	576.03	457.14	118.89	461.67
2	266.77	4.77	7.08	104.30	521.52	350.06	171.46	642.69

The pH of the effluent samples in columns 1 and 2 were measured throughout the experiments (Figure 9). The graph shows both columns eventually reached a stable 6-7 pH; however, the slope was steeper for the initial lower pH, possibly due to the strong pH gradient in column 1. Near the outlet, where pH is low after the initial humate injection, there may not only be precipitated HA, but also significantly more sorbed HA. As higher pH water moves through the zone, it dissolves the

precipitated HA and desorbs HA. Thus, there is a high concentration of HA eluting from column 2 than column 1 in the second pore volume, as seen in Figure 6. Concentration profile of HA in the effluent of the column. The higher HA concentration possibly has the buffering capacity to bind more protons in solution and raise the pH faster. This does not occur in column 2 as the pH gradient is much weaker.
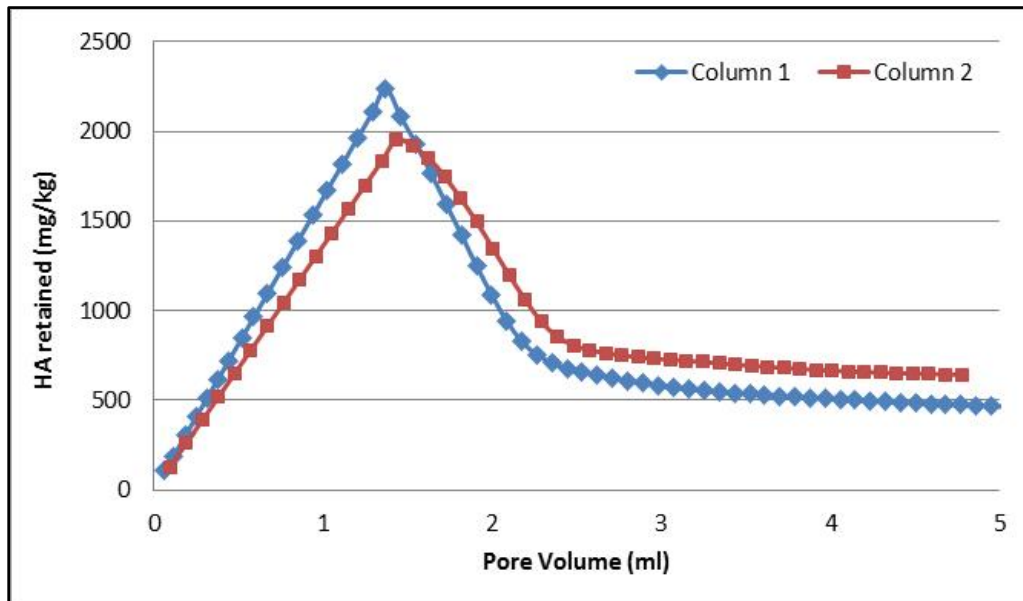

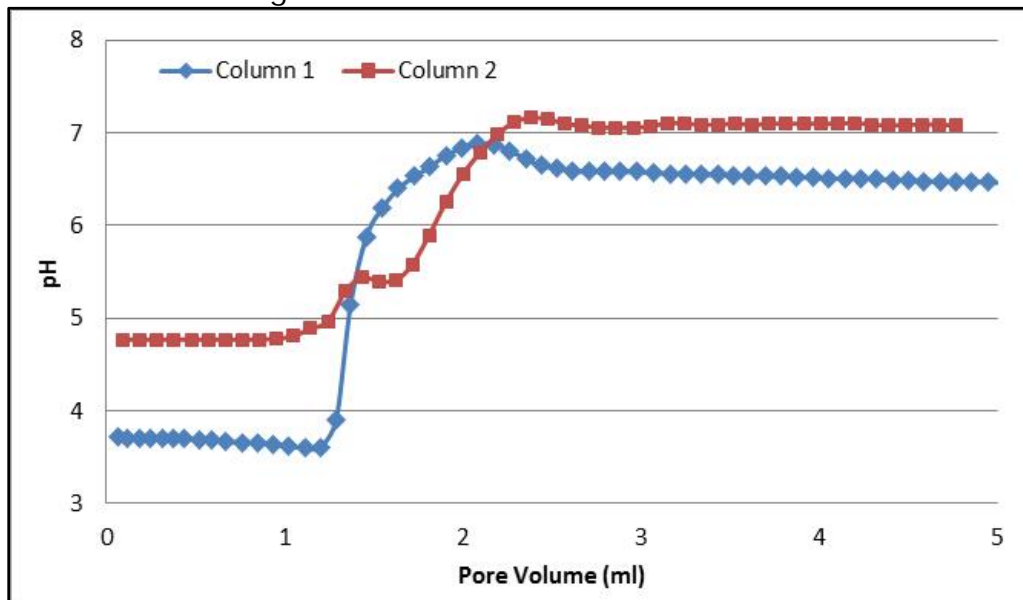Figure 8. Retention of HA in columns.

Figure 9. Change in pH of the columns.

The simple Langmuir model (Figure 2 - Figure 3), was used to observe how the HA injection scenarios differed from the actual column output curve. The peak concentration is 2500 ppm in the model and 6000 ppm in the experiment. The tail end concentration is 2000 ppm in the model and almost zero in the experiment.

The model did not account for precipitation and re-dissolution that may have occurred, which influences the deployment approach if results remain consistent. The model also assumes constant pH/parameters, while in the actual column, pH changes dynamically. The pH profile shows columns maintain 6-7 pH even after 4 PV of AGW have been injected, which can be considered in deployment for long term phases. Overall, the results demonstrate a realistic outcome and will be more useful for the development of a deployment model.

CONCLUSIONS

The transport of HA through subsurface systems was modeled by column experiments to observe the sorption and desorption characteristics at different pH. Overall, more HA was retained in column 2 preconditioned with a pH 5 AGW as compared to column 1 that was preconditioned with a pH 3.5 AGW solution. With an increase in pH from 3.5 to 5.0, the overall retention of HA increased by 180 mg per kg of soil, from 461 mg/kg in column 1 to 642 mg/kg for column 2. The results were different than what was expected due to the unanticipated effects of precipitation and dissolution due to mechanical and physicochemical factors. Sediments from columns will be collected, dried and characterized through scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). These analyses will provide the quantity of humate remaining on the surfaces of the soil particles for the levels within the column.

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