Project 3 - Task 1: Modeling of the Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems

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1.0 Introduction

The Savannah River Site (SRS) was one of the major U.S. Department of Energy (DOE) facilities for plutonium production during the Cold War. The F-Area Hazardous Waste Management Facility (HWMF) consists of three unlined, earthen surface impoundments, referred to as seepage basins. The F Area seepage basins cover approximately 6.5 acres. They received approximately 1.8 billion gallons (7.1 billion liters) of low-level waste solutions originating from the processing of uranium slugs and irradiated fuel in the F-Area Separations Facility from 1955 through 1988 (Figure 1). The low-activity waste solutions were acidic due to the presence of nitric acid and contained a wide variety of radionuclides and dissolved metals (Dong et al., 2012). Although the site has gone through many years of active remediation, the groundwater remains acidic with pH as low as 3.2 near the basins and increasing to a pH of approximately 5 downgradient; the concentrations of U(VI) and other radionuclides are still significantly higher than their maximum contaminant levels (MCLs).
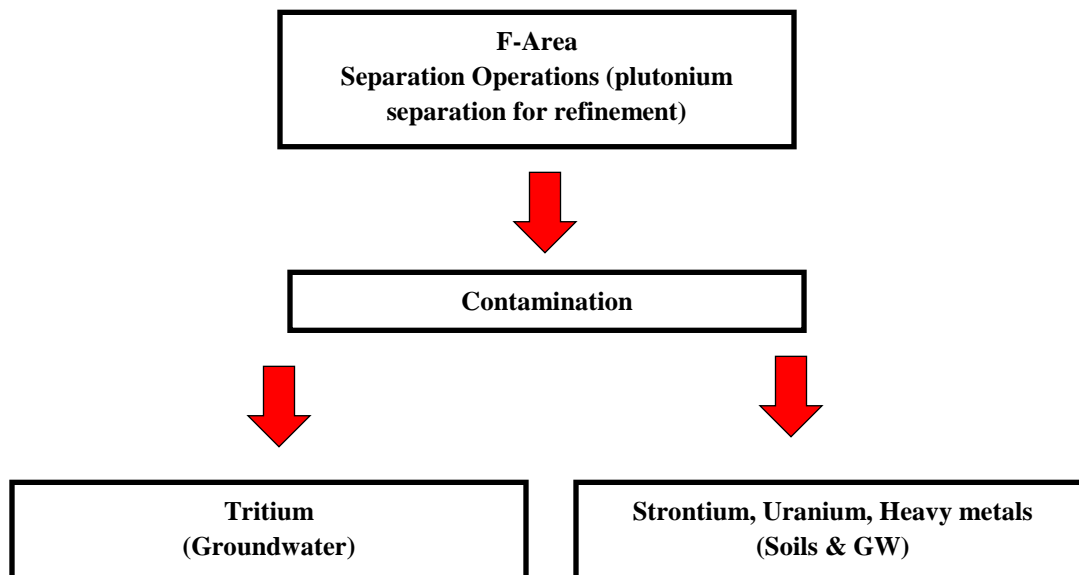
Figure 1. Source of contamination and contaminants

Millings et al. (2013) conducted a field test of a humic acid technology for uranium and iodine-129 (I-129) remediation at the F-Area Field Research Site and the data indicated that the test was successful in loading a band of sediment surrounding the injection point. Previous studies have also shown that humic acid (HA) sorbed to sediments strongly binds uranium at mildly acidic pH

and potentially binds I-129. Use of humic acid could be an appropriate technique to control the mobility of radionuclides at a wide variety of DOE sites; however, batch and column studies are required to optimize this approach and to ready it for actual field deployment and regulatory acceptance.
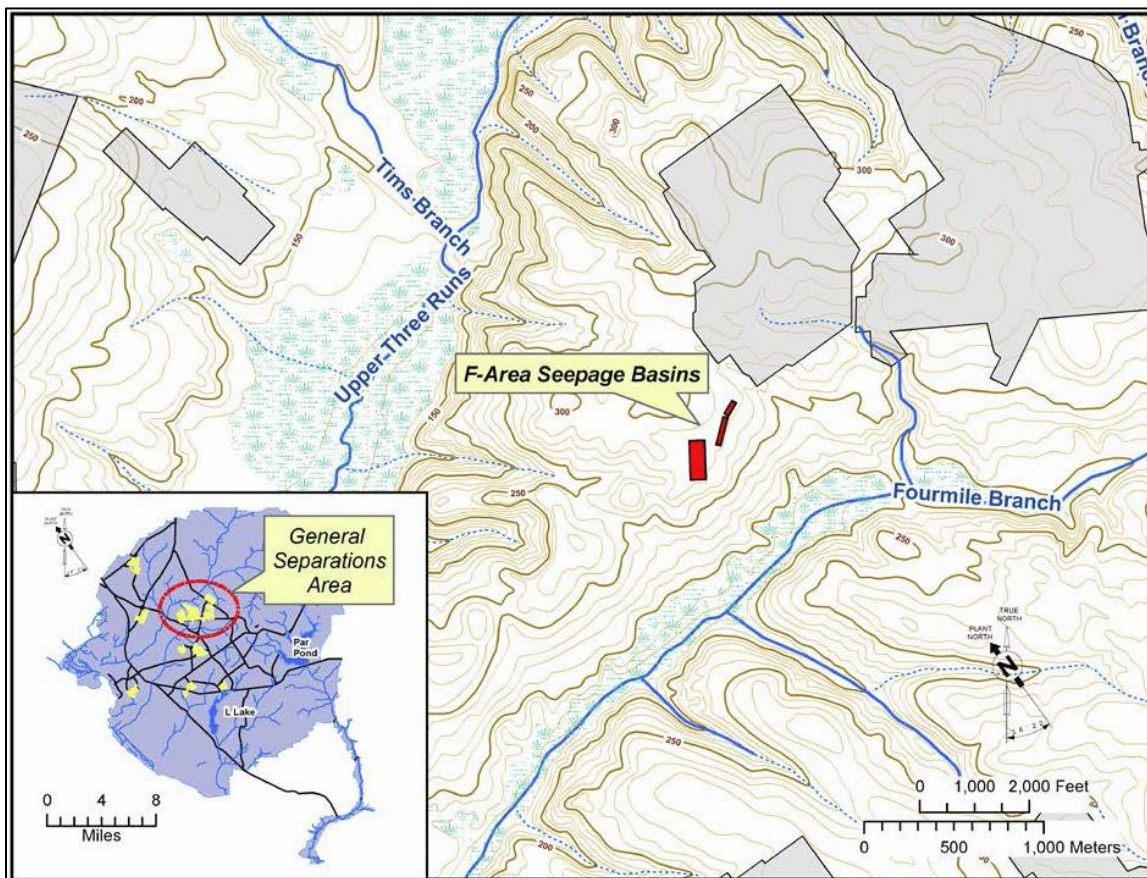
Figure 2. F-Area seepage basins (from Millings et al., 2013)

Humic substances (HS) are major components of the natural organic matter (NOM) in soil and water as well as in geological organic deposits. 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 in soils and sediments can be divided into three main fractions: humic acids (HA), fulvic acids (FA) and humin. The HA and FA can be extracted from soil and other solid phase sources using a strong base (NaOH or KOH). Humic acids are insoluble at low pH and they are precipitated by adding strong acid (adjust to pH 1 with HCl). Humin cannot be extracted with either a strong base or a strong acid.

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.

Understanding and development of strategies for effective deployment in the subsurface are essential to the success of humate-based technology concepts. Traditional models (e.g., Langmuir and Freundlich isotherms) can be used for sorption evaluation and will not be sufficient to provide all of the needed information for modeling. FIU-ARC is providing assistance to U.S. DOE-SRS in developing solutions to uranium (U) contamination in soil and will provide information on potential remediation technologies. The main objective is to develop an integrated model for the migration and distribution of natural organic matter injected into subsurface systems. To accomplish this goal, information on sorption and desorption of HA obtained via column experiments is needed.

2.0 Proposed Tasks

The proposed task describes laboratory experiments to be performed at the Applied Research Center (ARC) in support of uranium remediation at the Savanah River Site (SRS). The overall objective of this task is to obtain sorption/desorption parameters of humic substances (HS), specifically humic acid (HA) in SRS soil, to provide a better understanding of the mobility of HA injected into the acidic groundwater. During this study, commercially available Huma-K in the form of dry flakes will be used as the humate amendment because of its ease of use. The experimental work is designed to obtain sorption/desorption parameters of HA onto soil via flow-through column experiments. The experimental study will consist of two (2) major stages as outlined in the figure below:

Stage1
Estimation of
Parameters
(column size, flow
rates, etc.)

Stage2
Sorption and
Desorption
Column Studies

**Characterization
of SRS Soil**

**Column Tracer
Test**

Preconditioning
of the columns
with pH 3.5, 5, 6
and 7 solutions

Sorption
experiment with
Huma-K solution
with pH 9

Desorption
experiment with
pH 3.5, 5, 6 and
7 solutions
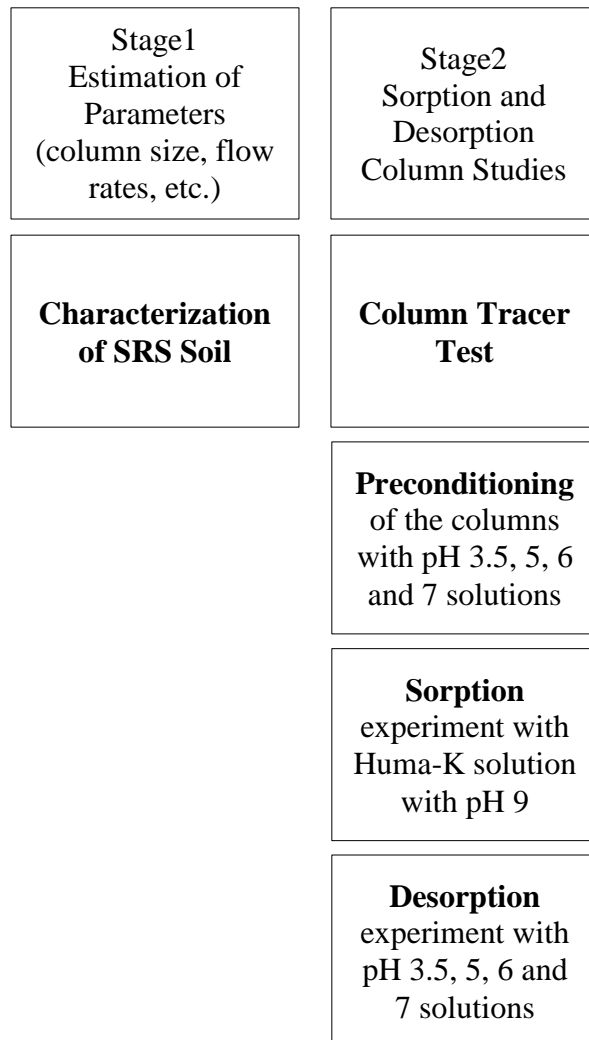
Figure 3. Study of humic acid sorption/desorption in SRS soil

3.0 Soil Characterization

Stage 1 of the experiments involves the estimation of flow rate and concentration of HA solutions needed for the experiments. The calculations will be based on the column size; the flow rate and concentration will be scaled-down to mimic the values used during the field test (Millings et al., 2013).

Soil obtained from SRS will be characterized prior to the column experiments. Soil will be sieved prior to use in the experiments using the following procedure:

- Disaggregate soil using minimal force to keep to avoid creating new mineral surfaces from fracturing and abrasionStack sieves having larger opening size over the smaller opening sieves over a pan
- Shake the sieves until all the soil passes through the sieves
- Collect all the sediment that passes through the 2-mm sieve as sediment of a particle size ≤2 mm.

3.1   Bulk Density Analysis

The bulk density (ρ_b) of a solid is defined as the ratio of the dry mass of the solid to its bulk volume. The bulk volume includes both the solid and void volume. The volume of the soil has to be measured without compaction, as it is taken from the field or as it is used in the lab studies. The mass of the solid will be determined after drying the known volume in a laboratory oven (Blake et. al., 1986).

The bulk weight of the solid amendment mixtures will be determined gravimetrically by using the following procedure:

1. Use triplicate samples.

2. Fill a 100-mL (can use smaller volume like 50 mL) beaker with soil mixture and note the volume.

3. Dry the mixture at $105^{o}C$ for one day until the weight is stabilized.

4. Determine the mass of the soil after cooling it in a desiccator.

Calculate the bulk density, ρ_b of soil by using the following equation:

$$Bulk\ Density\left(g\middle/cm^3\right)=\frac{Oven\ dry\ soil\ weight}{Volume\ of\ soil}$$

3.2   Particle Density Analysis

Particle density is the average density of the soil. The experimental procedures given in the *Methods of Soil Analysis for the Pycnometer Method* will be followed to determine the particle density of soil (Blake et. al., 1986):

1. Use triplicate samples.

2. Weigh 12.5 grams of air-dried soil sample

3. Introduce the soil sample to an oven-dried and pre-weighted 25 mL volumetric flask.

4. Add deinoized water (DIW) to the flasks until about one-half full.

5. Gently boil flasks with the solid slurry for a few minutes to eliminate air bubbles among the particles.

6. Cool down flasks.

7. Fill flasks to the 25 mL mark by adding from previously boiled and cooled DIW.

8. Measure the temperature of all of the samples (to ensure that all samples have the same temperature) and determine the final combined weights.

9. Discard soil + DIW mixtures and wash the flasks until all particle residues have been removed.

10. Fill the flasks with cooled-boiled DIW and weigh them again.

11. Determine particle density of the soil by using equation

$$\rho_p=\frac{\rho_w\left(W_s-W_a\right)}{\left[\left(W_s-W_a\right)-\left(W_{sw}-W_w\right)\right]}$$

12. Determine the water content of each sample in triplicate by drying at 105ºC

    Where:
    ρ_p - Particle density,

    ρ_w - Density of water in grams per cubic centimeter at temperature observed,

    W_s - Weight of pycnometer (flask) plus soil, corrected to oven-dry water content,

    W_a - Weight of pycnometer filled with air,

W$_{sw}$ - Weight of pycnometer filled with the soil and water slurry,

W$_{w}$ - Weight of pycnometer filled with water at temperature observed

3.3   Porosity

The measurement of porosity is described in *Methods of Soil Analysis* as the ratio of void volume of the soil to its total volume. The total porosity of the samples will be determined by using the equation (Danielson et. al., 1986):

$$Pt = 1 - \frac{\rho_b}{\rho_p}$$

Where:

ρ_p - Particle density,

ρ_b - Dry bulk density.

Porosity is a dimensionless quantity and is reported as a percentage or a decimal fraction. Data on soil porosity will be verified during the bromide tracer test.

3.4   Soil pHw

The soil sample pH in a 1:1 soil: water suspension will be determined. To measure the soil mixture pH, the following steps will be followed:

1. Place 10 g of soil and 10 mL of deionized water (DIW) into the triplicate beakers.

2. Stir the soil-DIW mixture for 15 minutes.

3. Let the mixed slurry stand for 15 minutes.

4. After the suspension has settled out, place the combination pH electrode in the clear supernatant and read the pH values of all soil samples.

5. Results will be expressed as pHw (soil pH measured in water).

4.0 Flow-through Column Experiments

The flow-through experiments will be used to determine various adsorptions/desorptions of humic acid (HA) and its transport parameters. Four (4) columns will be used during the experiments, each representing a specific pH. A given mass of the oven-dried soil will be placed in a glass column over a pure sand layer. Feed solution containing a known concentration of humic acid (Huma-K) will be injected into the column at a specific flow rate after pretreating the columns with pH (3.5, 5.0, 6.0 and 7.0) adjusted artificial groundwater solutions. The effluent solution will be collected at regular intervals until equilibrium is achieved (until the concentration of HA in the effluent reaches that of the influent). Desorption of HA will be studied after terminating the sorption experiments, pH (3.5, 5.0, 6.0 and 7.0) adjusted artificial groundwater solutions will be injected into the columns.

The hydraulic conductivity, Ks [m/s], will be determined by (Bear 1970):

$$K_s = \frac{A_t}{A_c} \frac{L}{T} \ln\left(\frac{H_i}{H_f}\right)$$

Where:

A_t - Cross sectional area of the falling head reservoir [m^2]

A_c - Cross sectional area of the column [m^2]

L - Length of the soil column [m]

T - Time for the fluid level to fall from H_i to H_f [s].

4.1   Artificial Groundwater (AGW) Recipe

Artificial groundwater (AGW) will be prepared to simulate the SRS groundwater plume; simulated groundwater will be prepared by following Wan et al. (2011, 2012), which involves mixing NaNO$_3$ to achieve a concentration of 0.01 M NaNO$_3$. 0.1 M HNO$_3$ and/or 0.1M NaOH solutions will be used to attain target pH values of 3.5, 5.0, 6.0 and 7.0.

Table 1. Composition of artificial groundwater solution

Compound	NaNO3
Amount added to 100 ml of deionized water (mg)	84.99

4.2   Column Tracer Test

Tracer testing is an integral investigation method as it allows the estimation of effective parameters describing non-reactive processes within an aquifer or aquifer material. Tracer tests can be performed under natural hydraulic gradient conditions in an undisturbed groundwater flow field, or under forced gradient conditions induced by groundwater pumping or groundwater/tracer solute injection. In the laboratory column experiments, a tracer solution is injected into a column and tracer breakthrough curves are measured by monitoring at column outlets (Figure 4). A variety of tracer compounds can be used depending on the site subsurface conditions; ideal tracers might be salt based tracers such as chlorides or bromides, or dye-based tracers such as fluorescent tracers (Ptak et al., 2004). A given mass of the oven-dried soil will be placed in a glass column over a pure sand layer (Ottawa Sand Standard, 20-30 mesh). Column tracer tests will use a mineral tracer, bromide, according to the following steps:

1. Fill columns with oven dried SRS soil; record soil weight

2. Saturated column with DI water from the bottom to the top

3. Determine flow rate that will provide approximately 1 inch of head

4. Add a pulse of spiked water containing bromide (10 mg)

5. Allow bromide solution to percolate through the sand layer to avoid dilution

6. Elute with DI water, added in small increments as a leaching solution

7. Maintain the flow rate and pressure in columns with a 1-inch water head above the top sand layer

8. Collect samples into pre-weighed containers until enough effluent is accumulated for bromide measurement using bromide electrode

9. Record volume of each collected sample

10. Collect samples until the bromide effluent concentration reaches zero to calculate Br recovery

11. Plot the bromide concentrations as a function of pore volume fraction

12. Normalize the concentration of bromide by dividing the mass of the tracer for each period by the total mass of added bromide

13. Determine the residence distribution function, E(v) as a function of volume fractions (Levenspiel, 1972)

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

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

14. Determine the mean residence time (t_m), and pore volume (V_p) (Shook et al., 2005):

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

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

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

15. Determine 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, by solving the 1D dispersion/advection equation (Bischoff et al., 1963; Fogler et al., 1992; Mibus et al., 2007):

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

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

Where:
v - Volume of effluent

v_p - Pore volume
$E(v)$ - Residence distribution function in terms of volume
t_m - Mean residence time

Bromide concentrations will be determined by a bromide electrode, which will be calibrated prior to each test to ensure the reliability and reproducibility of readings. A set of calibration standards in the range of 0.5 ppm to 50 ppm will be prepared using DI water and NaBr in 50-ml bottles.
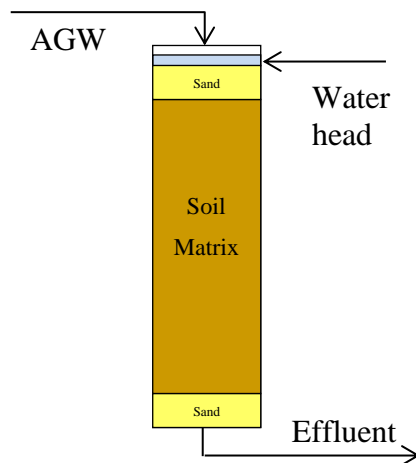

Figure 4. Tracer test experimental setup

4.3   Preconditioning of Soil Column

Preconditioning of the soil columns will be done to bring the soil pH to field conditions. The pH of soil at the F-area of SRS is 3.5; however, pH of 5.0, 6.0 and 7.0 will used in this study to expand the results for broader environmental conditions. The feed solution, containing different pH, will be pumped into the columns from the bottom to avoid the introduction of air bubbles. The effluent will be collected at regular intervals. The time when the effluent pH reaches that of the influent, equilibration is achieved. After the preconditioning of the columns, the flow direction will be reversed for the sorption/desorption experiments.

The procedure will consist of the following steps:

1. Prepare artificial groundwater with target pH (3.5, 5.0, 6.0 and 7.0)

2. Inject pH adjusted artificial groundwater solution into the columns from bottom of the column to avoid air bubbles.

3. Collect samples at regular intervals from the column outlet and measure pH.

4. Collect samples until pH is equal to influent pH.

Table 2. Preconditioning of columns

Column No.	pH of added water
1	3.5
2	5.0
3	6.0
4	7.0
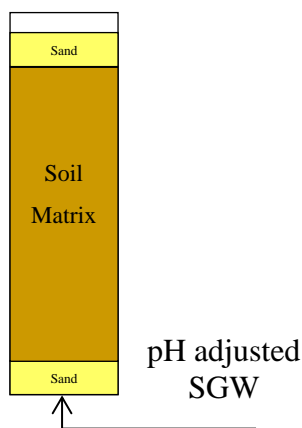
Figure 5. Preconditioning of soil column

4.4   Sorption Experimental Procedure

Once the preconditioning of the column is complete, humic acid solution at a known concentration and flow rate will be injected into the column from the top. The effluent will be collected at regular intervals and will be analyzed using a UV-Vis spectrophotometer. The experiment will be terminated once the effluent concentration reaches the influence concentration. The following steps will be followed:

1. Prepare humic acid (Huma-K) solution and adjust the pH to 9.0 using 0.1M HNO_3 and/or 0.1M NaOH.

2. Inject the humic acid solution into the columns at a predetermined flow rate.

3. Collect effluent samples at regular intervals, measure the concentration of HA and pH in the effluent.

4. Terminate the experiment once the effluent concentration reaches the influent concentration.

5. Determine the equilibrium concentrations by plotting the concentration of HA in effluent (ppb) vs. amount of HA adsorbed in mg/kg of soil.

6. Compare the HA adsorption from batch and flow-through tests.

4.5   Desorption Experimental Procedure

After the adsorption experiments are complete, desorption of HA will be studied by pumping pH adjusted artificial groundwater through the columns and effluent samples will be collected at regular intervals until the pH of the effluent solution reaches the pH of the inlet solution. The following steps will be followed:

1. Prepare fresh artificial groundwater with pH of 3.5, 5.0, 6.0 and 7.0.

2. Inject pH 3.5, 5.0, 6.0 and 7.0 groundwater solutions into respective columns.

3. Collect samples at regular intervals from the column outlet and measure pH.

4. Collect samples until pH is equal to influent pH or after at least three (3) pore volumes.

5. Measure concentration of HA in the effluent.

6. Calculate the amount of HA injected vs. eluted at each pH.

5.0 Results

All the experimental data will be recorded and reviewed for accuracy; all experimental observations will be documented in the Logbooks including date, time of the experiments and sample information. They will be retained for legal and knowledge preservation purposes.

Initial results of these experiments will be included in the project monthly and quarterly reports. Final results, conclusions, and recommendations will be detailed in the Technical Report for Task 1. Furthermore, results will be discussed with site point of contact on a bi-weekly basis and experiments will be modified, if necessary, based on the discussion.

6.0 Instrumentation, Chemicals and Reagents

The following instruments and equipment will be used during the experiments and analysis:

- Thermo Scientific Genesys^{TM} 10S UV-Vis spectrophotometer

- pH/ISE Meter

- Bromide Electrode (will be selected prior to tracer test)

- Chemicals and Reagents

  - Huma-K, sample obtained from SRS

  - $NaNO_3$, ACS reagent grade

  - HNO_3, ACS reagent grade

  - NaOH, ACS reagent grade

  - NaBr, ACS reagent grade bromide standard

7.0 Health and Safety

All project activities will be performed in accordance with ARC and FIU's safety plan. All personnel working in the laboratory will complete health and safety trainings required and offered by FIU environmental health and safety (EH&S) and training certificates will be displayed in the laboratory for review. All tasks will be conducted in accordance with OSHA guidelines including the personal protective equipment.

Other hazards are common to all laboratory environments and include exposure to strong acids or bases, slips on wet flooring, injuries due to broken glass or plastic parts, pinches or punctures while dealing with equipment. An eye wash chamber and a shower are located near the work areas for quick drenching to minimize the dangers due to chemical exposure.

8.0 Waste Disposal

The waste products generated during these experiments by ARC will be handled and disposed of in accordance with the FIU waste management program. All accumulated waste will be stored in specified locations, in labeled receptacles with appropriate spill containers. Soil will be disposed according to USDA regulations after heating to soil to 250 $^{\circ}$C in a furnace.

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