DOE-EM Cooperative Agreement FIU Performance Year 6 Research Review

Presented: April 5 - April 7, 2016
to the U.S. Department of Energy
Dr. Leonel Lagos, PhD, PMP® (Principal Investigator)

FLORIDA INTERNATIONAL UNIVERSITY

FIU-DOE Research Review

Tuesday April 5, 2016	Wednesday April 6, 2016	Thursday April 7, 2016
1:00-2:30 High Level Waste / Waste Processing (FIU Project 1)	10:00-12:00 Workforce Development & Training (FIU Project 4)	10:00-12:00 Wrap Up (All Projects)
2:30-4:00 D&D/IT for EM (FIU Project 3)	**1:00 - 3:00** **Soil/Groundwater** **(FIU Project 2)**	

Project 2
Environmental Remediation Science & Technology

Florida International University

Project Staff and Students

Faculty/Staff:

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- Dr. Ravi Gudavalli
- Dr. Yelena Katsenovich
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Project Clients and Collaborators

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DOE HQ (EM-12/13) Collaborators:	Skip Chamberlain
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Project Description

This project involves research that supports the resolution of critical science and engineering needs, leading to a better understanding of long-term behavior of contaminants in the subsurface. Tasks include:

- Novel analytical methods and microscopy techniques for characterization of various mineral and microbial samples.
- Studies which predict the behavior and fate of radionuclides that can potentially contaminate the groundwater system in the Hanford Site 200 Area.
- Laboratory batch and column experiments, which provide relevant data for modeling of the migration and distribution of natural organic matter injected into subsurface systems in the SRS F/H Area.
- Surface water modeling of Tims Branch at SRS supported by the application of GIS technology for storage and geoprocessing of spatial and temporal data.
- Use of state of the practice tools to conduct a sustainable remediation analysis of the SRS M1 Air Stripper and to provide sustainable remediation support for the DOE EM student challenge.
- Laboratory experiments investigating the behavior of the actinide elements in high ionic strength systems relevant to the Waste Isolation Pilot Plant (WIPP).

Project Description

Task 1: Remediation Research and Technical Support for the Hanford Site

Subtask 1.1 Sequestering uranium at the Hanford 200 Area vadose zone by in situ subsurface pH manipulation using NH_3 gas

Subtask 1.2 Investigation of microbial-meta-autunite interactions - effect of bicarbonate and calcium ions

Subtask 1.3 Evaluation of ammonia fate and biological contributions during and after NH_3 injection for uranium treatment

Task 2: Remediation Research and Technical Support for Savannah River Site

Subtask 2.1 FIU's support for groundwater remediation at SRS F/H Area

Subtask 2.2 Monitoring of U(VI) bioreduction after ARCADIS demonstration at the SRS F-Area

Subtask 2.3 Humic acid batch sorption experiments into the SRS soil

Subtask 2.4 The synergetic effect of HA and Si on the removal of U(VI)

Subtask 2.5 Investigation of the migration and distribution of natural organic matter injected into subsurface systems

Task 3: Surface Water Modeling of Tims Branch

Subtask 3.1 Modeling of surface water and sediment transport in the Tims Branch ecosystem

Subtask 3.2 Application of GIS technologies for hydrological modeling support

Subtask 3.3 Biota, biofilm, water and sediment sampling in Tims Branch

Task 4: Sustainability Plan for the A/M Area Groundwater Remediation System

Subtask 4.1 Sustainable Remediation Analysis of the M1 Air Stripper

Subtask 4.2 Sustainable Remediation Support to DOE EM Student Challenge

Task 5: Remediation Research and Technical Support for WIPP

DOE-FIU Cooperative Agreement

Project 2 Accomplishments

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Task 1:
Remediation Research and Technical Support for the Hanford Site

Florida International University

Task 1: Background

- A significant portion of rad waste legacy materials resides within the VZ.
- This contamination created plumes that threaten GW quality due to potential downward migration through the unsaturated VZ.
- Sequestration of radionuclides such as U(VI) in the VZ is more cost effective than GW remediation.
  - The technology under consideration is a manipulation of sediment pH via ammonia gas injection to create alkaline conditions in the uranium-contaminated sediment.
  - Investigate the potential biological and physical mechanisms associated with the fate of ammonia after injection into the unsaturated subsurface.
- Tripolyphosphate injections is a method to decrease the concentration of soluble U(VI) in contaminated plumes at the Hanford Site.
  - Bacteria can affect uranium mobility and may dissolve uranyl-phosphate minerals to obtain phosphorous for their metabolism.

Subtask 1.1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH_3 Gas

Solid phase characterization studies

Dr. Yelena Katsenovich
Claudia Cardona (DOE Fellow)
Robert Lapierre (DOE Fellow)

Florida International University

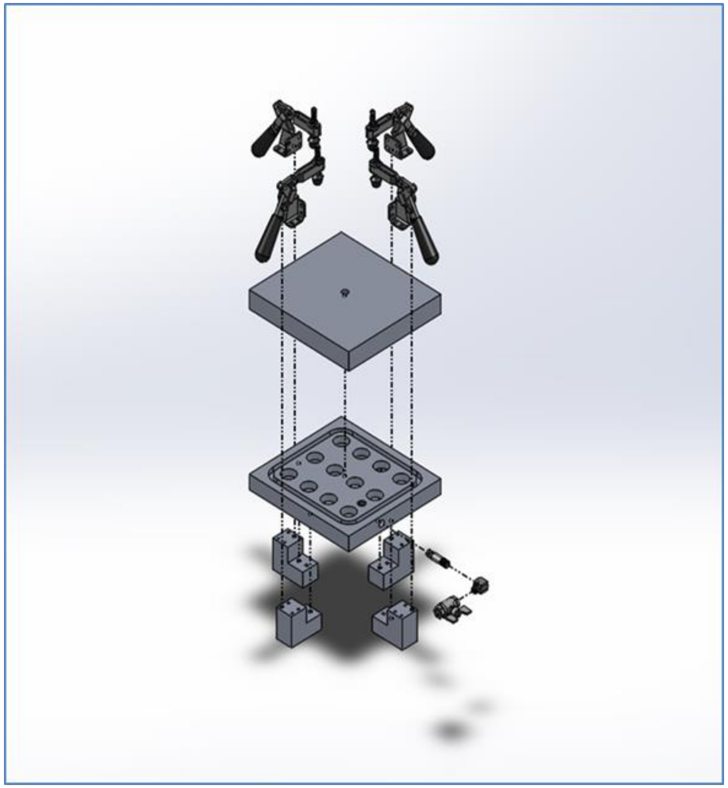
Subtask 1.1: Objectives

- Evaluate the stability of U-bearing precipitates created after NH_3 (5% NH_3 in 95% N_2) pH manipulation in the synthetic solutions mimicking conditions found in the VZ at the Hanford Site 200 Area.
- Examine the deliquescence behavior of formed uranium-bearing solid phases via isopiestic measurements.
- Investigate the effect of environmental factors relevant to the Hanford vadose zone on the solubility of solid phases.
- Continue to analyze mineralogical and morphological characteristics of precipitates by means of XRD and SEM-EDS.

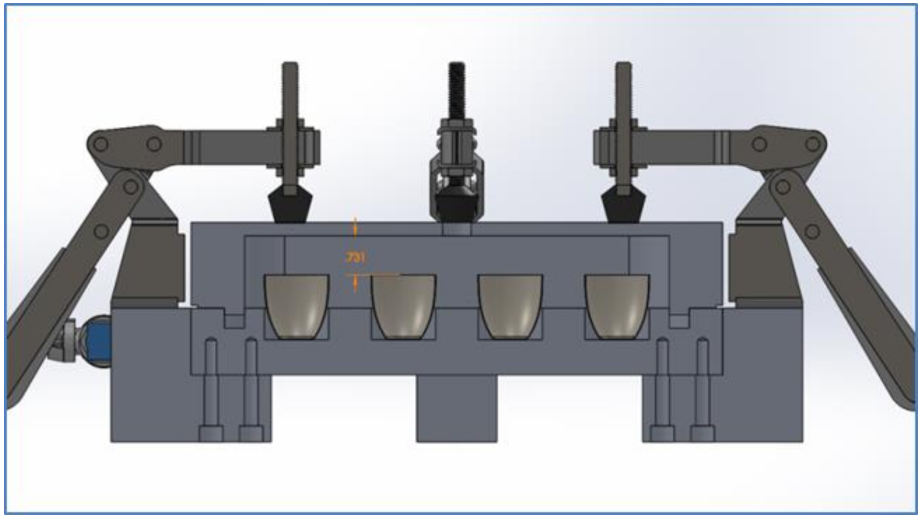
Subtask 1.1: Isopiestic Measurements

- Isopiestic measurements on the deliquescence behavior of multicomponent U-bearing samples:
  - The isopiestic method is based on equilibration of a number of solutions together with reference standards in a common chamber until all solutions reach the same water activity.
  - Only the solvent is exchanged between samples.
  - The masses of non-volatile solutes placed in the crucibles remain constant.
  - The amounts of water present at any time and the molalities of the solutions can be determined gravimetrically at the equilibrium.
- The deliquescence behavior of multicomponent precipitates help to understand solid–liquid transition when mixture of initially dry salts starts deliquescence.

Subtask 1.1: Isopiestic Chamber

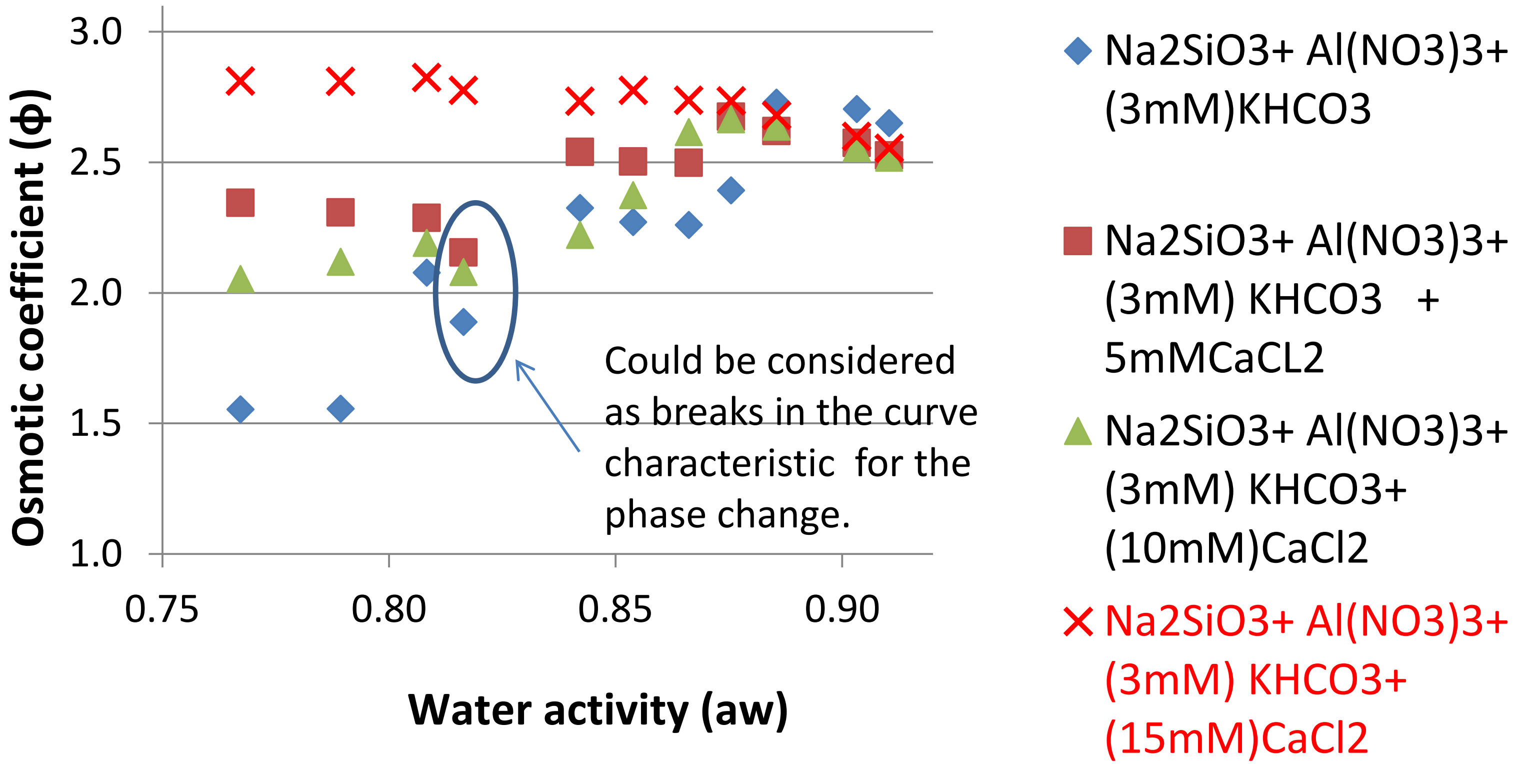


Isopiestic chamber final assembly.



The full assembly of the isopiestic chamber with crucibles inside to obtain osmotic and activity coefficients for aqueous solutions.

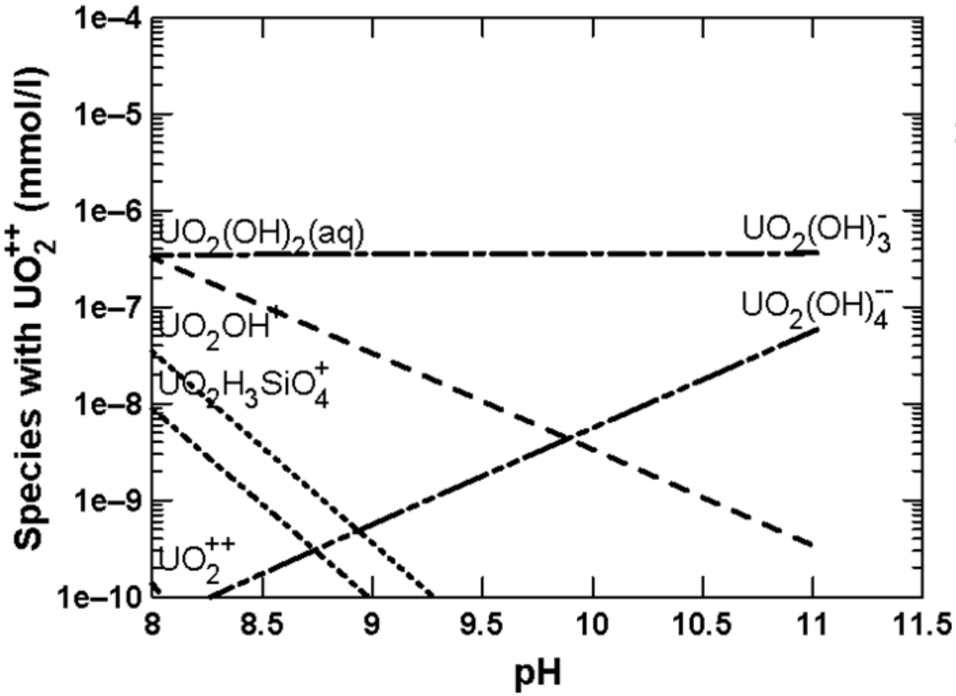
Subtask 1.1: Results on Solid–Liquid Transition

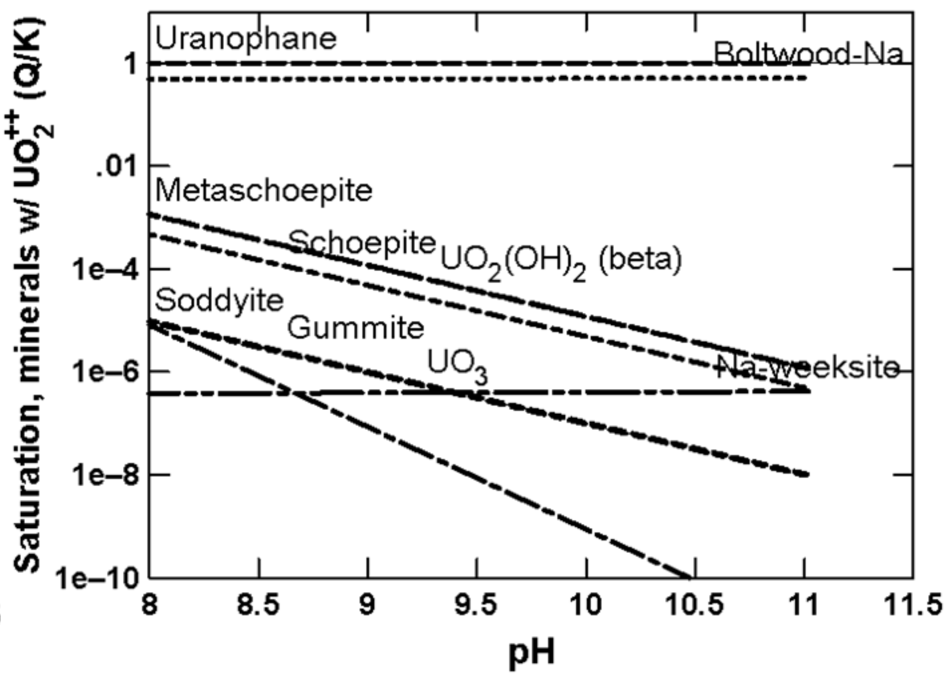


So far, there are no breaks in the curve for the sample composed of 3mMHCO_3 and 15mMCa sample. This can be considered that this sample is the most stable with respect to solid–liquid transition (marker in red). The deliquescence point depends on the sample composition.

Subtask 1.1: Results on Speciation Modeling

Updated GWB database to include thermodynamic data on U-solid phases.

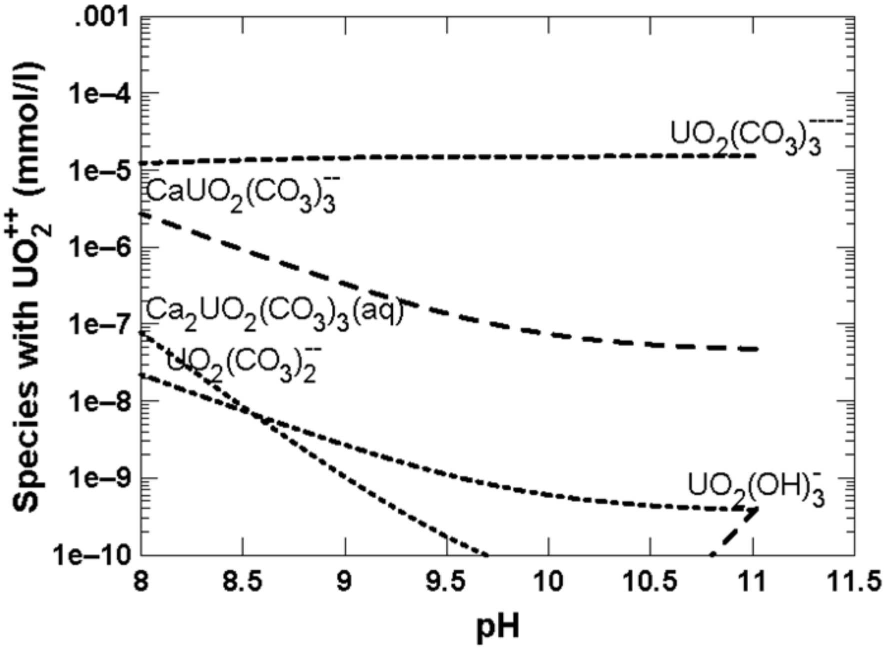




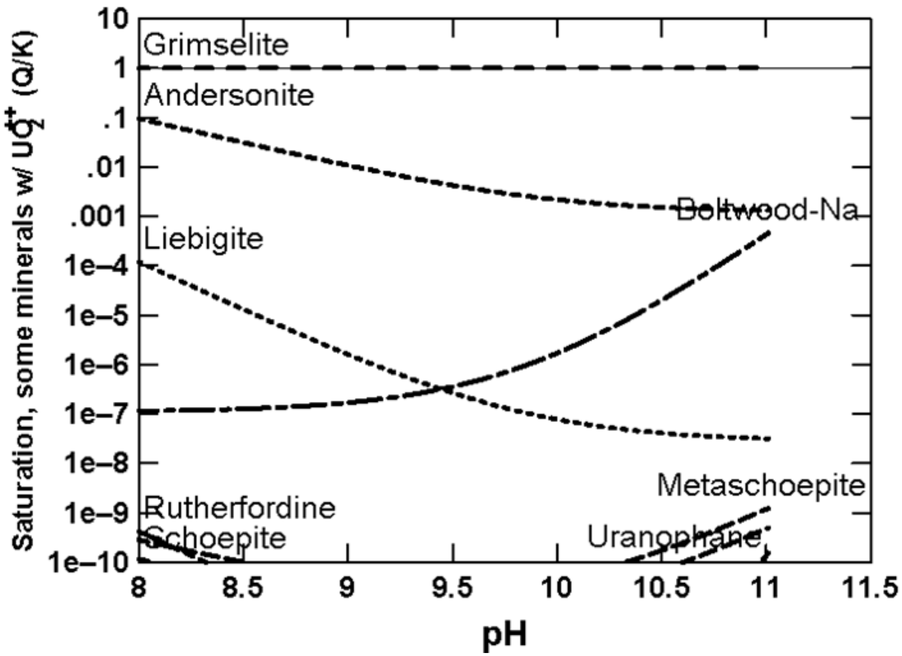
Sample composition includes 2ppm of U(VI), 50mM of Si, 10mMCa, and 0 mM HCO_3

Subtask 1.1: Results on Speciation Modeling

Uranium Species



Mineral saturation indexes



Sample composition includes 2ppm of U(VI), 50mM of Si, 10mMCa, and 50mM HCO_3.

Subtask 1.1: Sequential Extraction

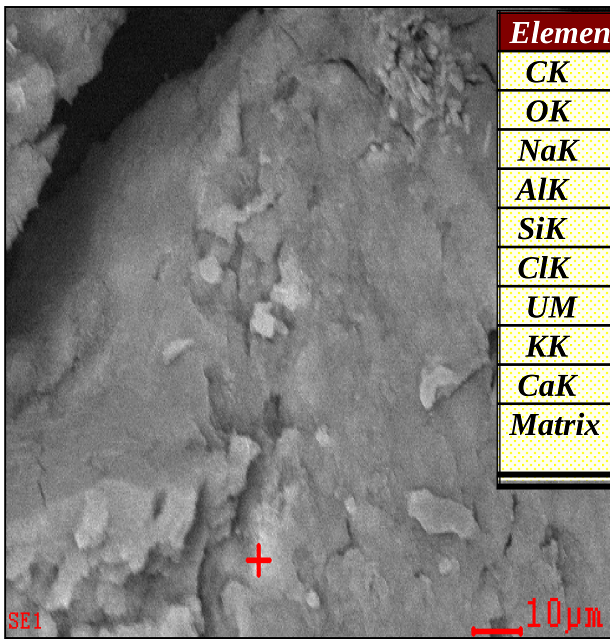
- Prepared a total of 24 samples (duplicate filtered and unfiltered) for the sequential extraction experiments.

50Si + 5Al + 3HCO_3 + 0Ca + 2 ppm U
50Si + 5Al + 3HCO_3 + 5Ca + 2 ppm U
50Si + 5Al + 3HCO_3 + 10Ca + 2 ppm U
50Si + 5Al + 50HCO_3 + 0Ca + 2 ppm U
50Si + 5Al + 50HCO_3 + 5Ca + 2 ppm U
50Si + 5Al + 50HCO_3 + 10Ca + 2 ppm U

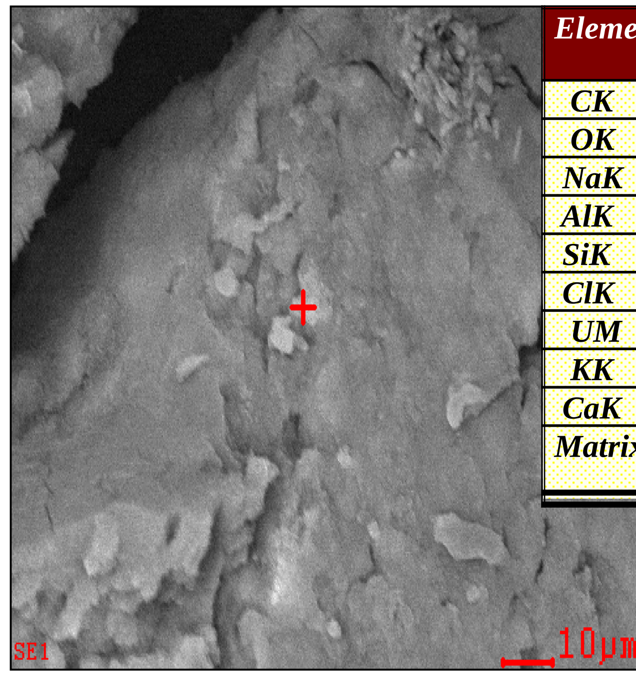
Task will follow PNNL extraction procedures outlined in 6 steps (Szecsody et al, 2015).

Subtask 1.1: SEM/EDS Analysis

3mMSi+5mMAl+3mMHCO_3+5mMCa+500ppm of U(VI)



Element	*Wt%*	*At%*
CK	06.82	13.14
OK	37.00	53.53
NaK	03.90	03.93
AlK	02.39	02.05
SiK	29.65	24.44
ClK	00.47	00.31
UM	18.38	01.79
KK	00.84	00.49
CaK	00.55	00.32
Matrix	Correctio n	ZAF



Element	*Wt%*	*At%*
CK	07.28	13.03
OK	38.87	52.19
NaK	03.96	03.70
AlK	04.11	03.27
SiK	33.70	25.78
ClK	00.32	00.19
UM	10.07	00.91
KK	01.07	00.59
CaK	00.62	00.33
Matrix	Correction	ZAF

“Hot” spots are high in Si and U. No crystals observed compared to previous non-filtered samples preparation. Results correlate with speciation modeling.

Subtask 1.1: Uranium Stability Experiments Future Work

- Complete sequential extraction experiments.
- Initiate flow through solubility experiments.
- Finalize deliquescence experiments at 25°C.

Subtask 1.1: Solid Phases Characterization. Experimental Methodology

- Sample preparation methods were modified to minimize formation of errant phases.
  - Vacuum Filtration
  - DI-Water Rinse

Subtask 1.1: Solid Phases Characterization. Experimental Methodology

- Carried out optimization study to maximize uranium analyte in precipitate phases.
  - Combinations of low, mid, and high concentrations of two key variables (Ca^{2+} & HCO_3^-).

	$[Ca^{2+}]$	$[HCO_3^-]$
Low	0	5
Mid	5	25
High	10	50

Subtask 1.1: Solid Phases Characterization. Experimental Methodology

- The varying synthetic pore water solutions were treated using NH_3 remediation method.
  - pH elevated to 11-12 range
    - Monitored reestablishment of pH ~8 over 2 months

Subtask 1.1: Solid Phases Characterization. Experimental Methodology

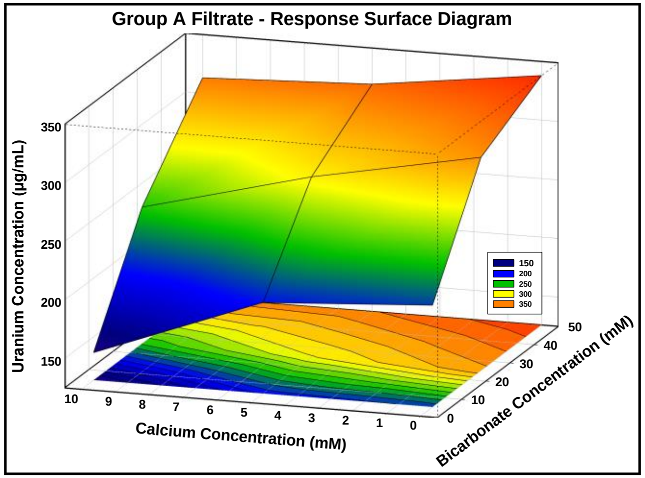
- The precipitate and aqueous phases were isolated for analysis by vacuum filtration.
    - Duplicate samples were rinsed with 5mL DIW.
- Solid phases dried in a temperature controlled incubator over 3 days.

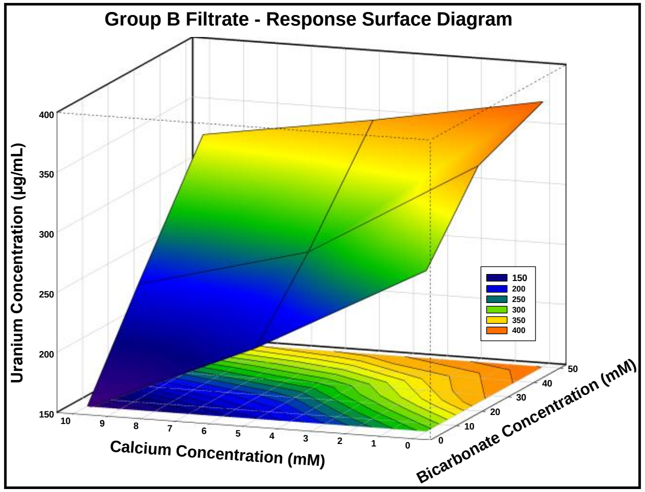
Subtask 1.1: Solid Phases Characterization. Experimental Methodology

- Filtered supernatant and rinse solutions were diluted 100,000 times and evaluated for uranium concentration by KPA.
- Small specimens from the dried precipitates are isolated for SEM-EDS analysis.
  - Backscatter electron capture specifically is used to visually distinguish areas of elevated uranium content.
- Samples with discernible uranium-bearing structures are selected for further analysis.
  - XRD analysis for the determination crystal structure.
  - EPMA analysis for the stoichiometric estimation of structural formula.

Subtask 1.1: Solid Phases Characterization. Results

- The resulting KPA data was used to prepare response surface diagrams.
  - The diagrams for the samples (Group A) and their duplicates (Group B) show a consistent trend between analyte and variable.
    - High bicarbonates are associated with high levels of uranium in solution.
    - High calcium samples are associate with the lowest levels of uranium in solution.

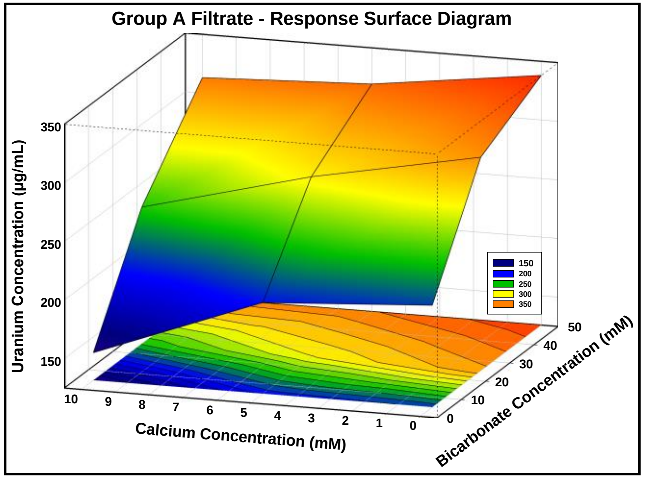


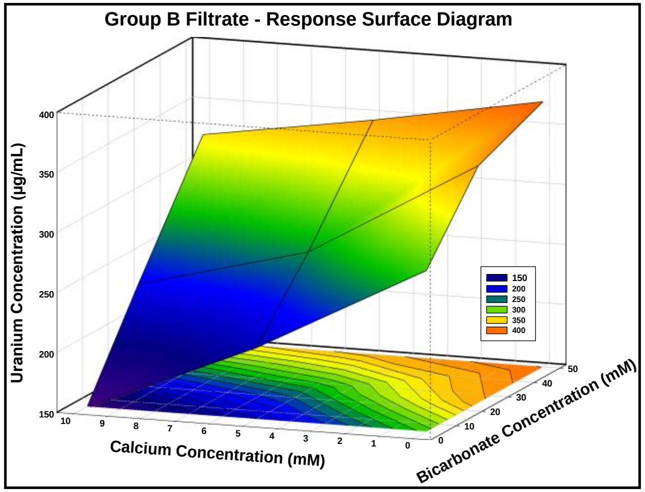


*not shown: KPA data for rinse solutions

Subtask 1.1: Solid Phases Characterization. Results

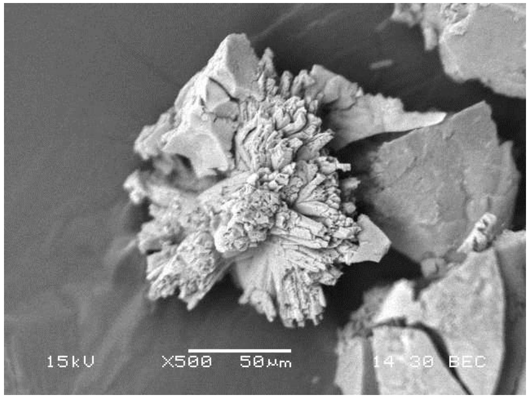
- Based on the assumption that precipitation is the only cause of uranium removal from solution data implies that:
    1. The high calcium, low bicarbonate samples, showing the least uranium retained in solution, would have the most uranium in the solid phase.
    2. The low calcium, high bicarbonate samples, having the most uranium in solution, should have the least in the solid phase.



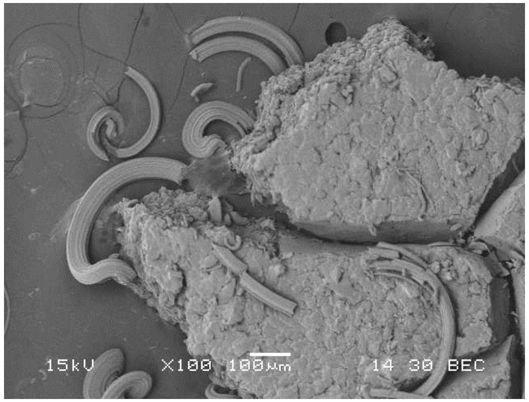


Subtask 1.1: Solid Phases Characterization. SEM/EDS Results

- SEM & EDS data
  - Interesting formations; particularly in higher HCO_3^- samples.
  - EDS data and prior experiments suggest that these are likely $CaCO_3$ (top) and $NaNO_3$ (bottom).
- None of the uranyl forms observed in the past analysis were spotted.



Element	Wt%	At%
C K_α	18.43	28.04
N K_α	03.11	04.05
O K_α	46.75	53.41
Na K_α	00.73	00.58
Al K_α	00.08	00.06
Si K_α	00.19	00.13
U M_α	00.70	00.05
Ca K_α	30.01	13.69



Element	Wt%	At%
C K_α	03.30	04.82
N K_α	16.02	20.08
O K_α	42.34	46.46
Na K_α	36.79	28.10
Al K_α	00.26	00.17
Si K_α	00.35	00.22
U M_α	00.72	00.05
Ca K_α	00.21	00.09

Subtask 1.1: Solid Phases Characterization. SEM/EDS Results

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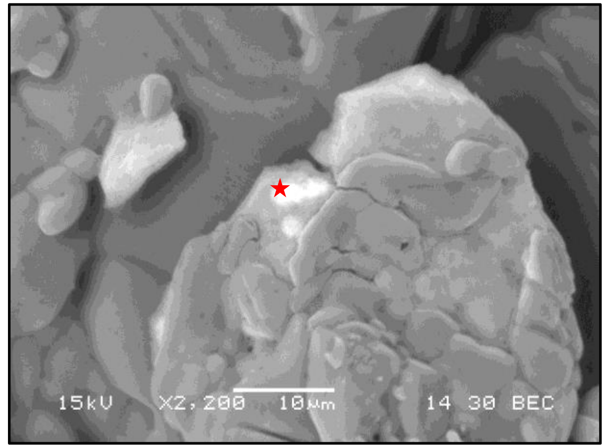
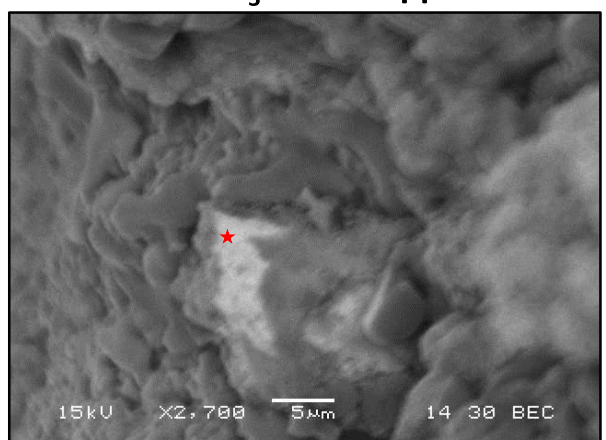
- The uranium rich sites were exclusive to the high bicarbonate samples.
    - SEM-EDS data shows hotspots for high HCO_3^- samples with low (top) and mid (bottom) level calcium content.
    - Contradicts the KPA data.



Element	Wt%	At%
C K_α	06.33	11.22
N K_α	03.61	05.48
O K_α	41.41	55.08
Na K_α	06.60	06.11
Al K_α	01.78	01.40
Si K_α	25.58	19.38
U M_α	14.69	01.31

SEM image w/ EDS data for specimen 50-00A, prepared using a 50mM of HCO_3^- and 200ppm uranium pore water solution

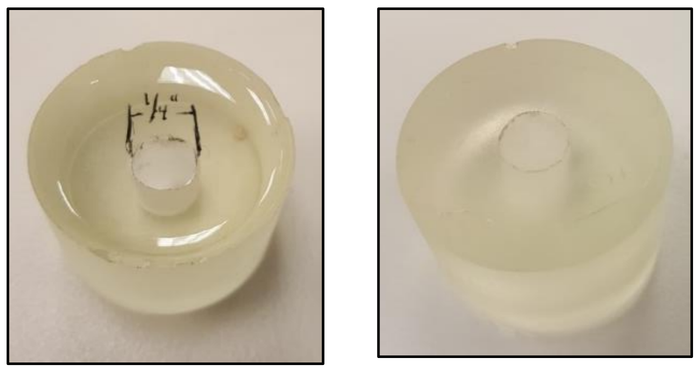


Element	Wt%	At%
C K_α	06.96	12.37
N K_α	04.68	07.13
O K_α	39.29	52.44
Na K_α	11.00	10.22
Al K_α	01.59	01.26
Cl K_α	00.91	00.55
Si K_α	19.05	14.48
U M_α	16.40	01.47
Ca K_α	00.12	00.06

SEM image w/ EDS data for specimen 50-05A, prepared using a 50mM of HCO_3^-, 5mM Ca^{2+}, and 200ppm uranium pore water solution

Subtask 1.1: Solid Phases Characterization Future Work

– Sample preparations for additional analysis of select solid samples (EMPA/TEM)



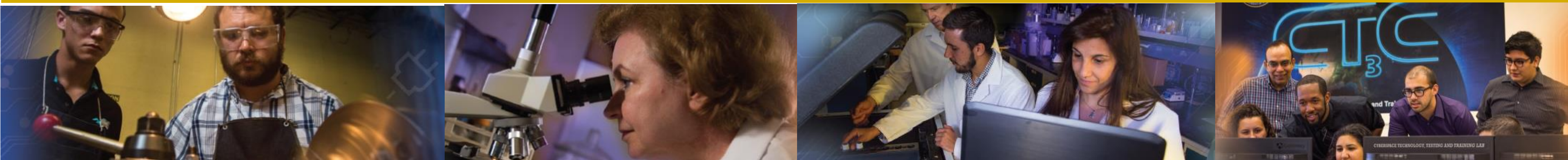
Epoxy mold before (L) and after (R) sample additions

– Digestions of solid samples for compositional analysis (KPA/ICP)

Subtask 1.2. Investigation of Microbial-Meta-Autunite Interactions

Dr. Vasileios Anagnostopoulos
Dr. Yelena Katsenovich
Sandra Herrera (Graduate Student)

Florida International University



Subtask 1.2: Background

- The injection of sodium tripolyphosphate into uranium-bearing saturated porous media results in the formation of uranyl phosphate solid phases (autunite).
- Soil bacteria affect uranium mobility significantly in an effort to obtain phosphorous.
- The Columbia River exhibits large stage variations, causing fluctuations in the water table.
  - Water table fluctuations and multiple rise-and-fall cycles in the river created an oxic-anoxic interface in this region.

Subtask 1.2: Objectives

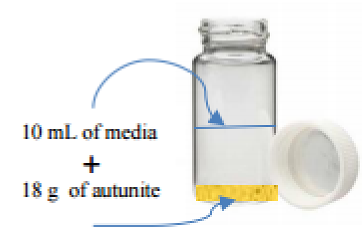
- Investigate autunite biodissolution under anaerobic conditions by focusing on bacterial strains *Shewanella oneidensis MR1* sp.
  - Research the effect of various concentrations of bicarbonate on biorelease of U(VI) from autunite.

Subtask 1.2: Experimental Methodology

- Obtained *Shewanella oneidensis MR1* strain from the PNNL
- Preserved culture in 25% glycerol at -80°C prior to use.
- Used sterile hard and liquid Luria-Bertani (LB) media for culturing.
- Performed autunite biodissolution experiments using 20-mL sacrificial glass scintillation vials.
  - To avoid microbial cross- contamination during sampling events.
- Weighed 18 mg of autunite powder in each vial to provide 4.4 mmol/L of U(VI) concentration.
- Amended each vial with 10 mL of sterile media solution containing 0, 3, and 10 mM $KHCO_3$.
  - The total number of vials was 99, duplicate vials and abiotic control for each HCO_3 concentration.
- Inoculated each vial with the initial cell density of 10^6 cells/mL, control vials were bacteria-free.

Subtask 1.2: Experimental Methodology

Sacrificial vials inside the anaerobic glove box



20-mL glass scintillation vial prepared with media amended with $KHCO_3$ and autunite mineral

								inoculation																																
Sampling	Day 3			Day 7			Day 10			Day 14			Day 17			Day 21			Day 25			Day 25			Day 35			Day 39			Day 44			Day 50			Day 56			Tot
Abiotic	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	
Biotic					Duplicates					●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	
										●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	
# vials	1	1	1	1	1	1	1	1	1	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	99

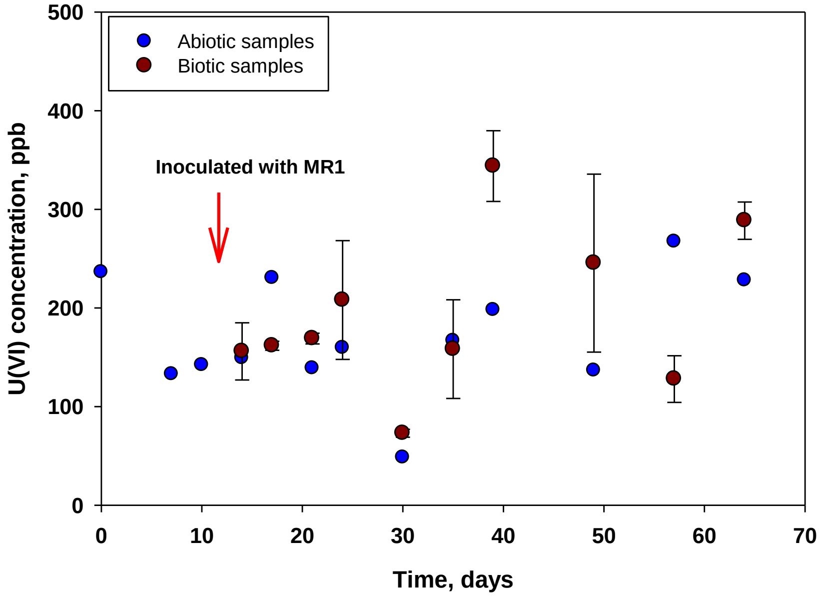
Legend

0mM	(yellow)
3mM	(green)
10mM	(blue)

Sampling schedule before and after inoculation.

Subtask 1.2: Results on U(VI) Biorelease in HCO3-free Samples

- BCA (Pierce) protein analysis
- Hemocytometer to calculate cells density
- Petri dish plating for calls viability
- SEM/EDS analysis
- U(VI) analysis via KPA
- Ca and P analysis via ISP-OES
- Visual Minteq and Hydra for speciation modeling



In bicarbonate-free samples

- U(VI) released was not statistically significant between abiotic and biotic samples
- *Shewanella* does not contribute to the release of U(VI) in the aqueous phase.

Subtask 1.2: Results on U(VI) Biorelease

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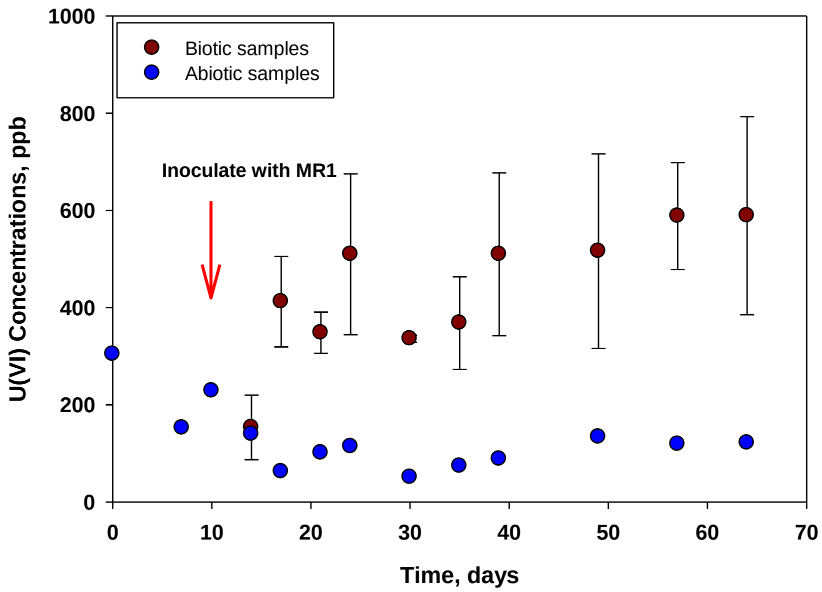
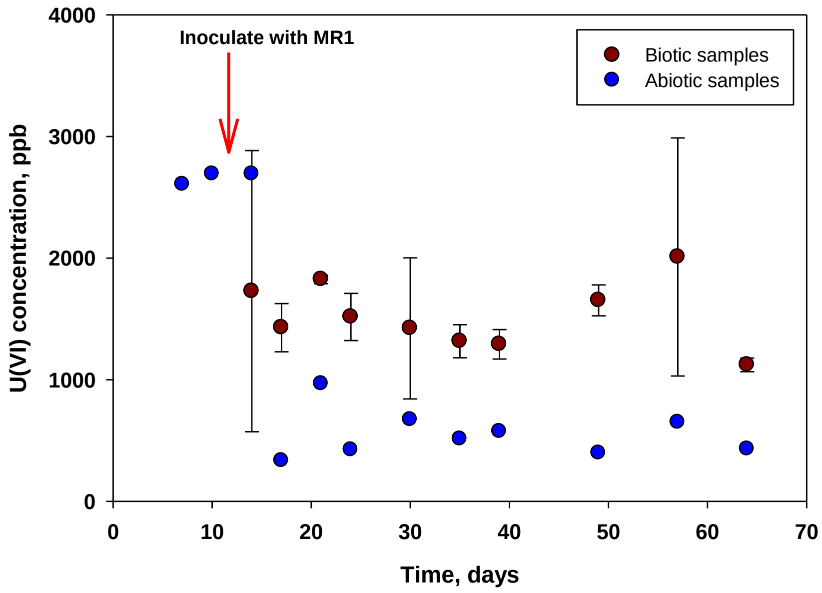
U(VI) vs. Time for samples amended with 3 mM HCO_3



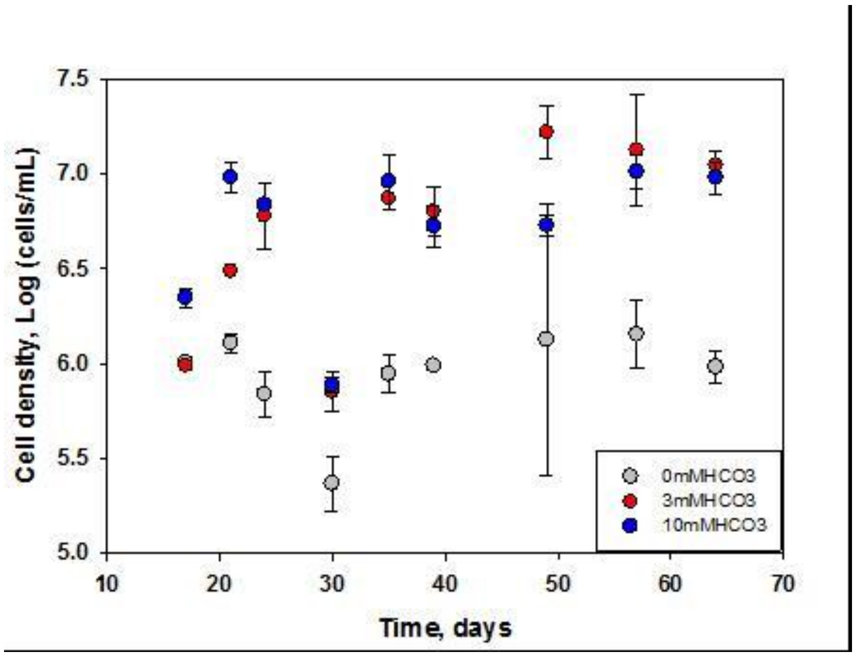
U(VI) vs. Time for samples amended with 10 mM HCO_3



- No U(VI) bioreduction was observed in any of the conditions studied.
- Noted a progressive increase in uranium release as the concentration of bicarbonate in the sample increased.

Subtask 1.2: ICP Results/ Cell Density Changes

- A similar trend for biotic and abiotic samples for Ca and P analysis.
  - Not a statistically significant difference between abiotic and biotic samples
- In HCO_3^--free samples, cell densities showed almost no change from the initial concentration .
- 3 mM and 10 mM HCO_3^- amended samples demonstrated almost 10-14 fold increase in cells density.

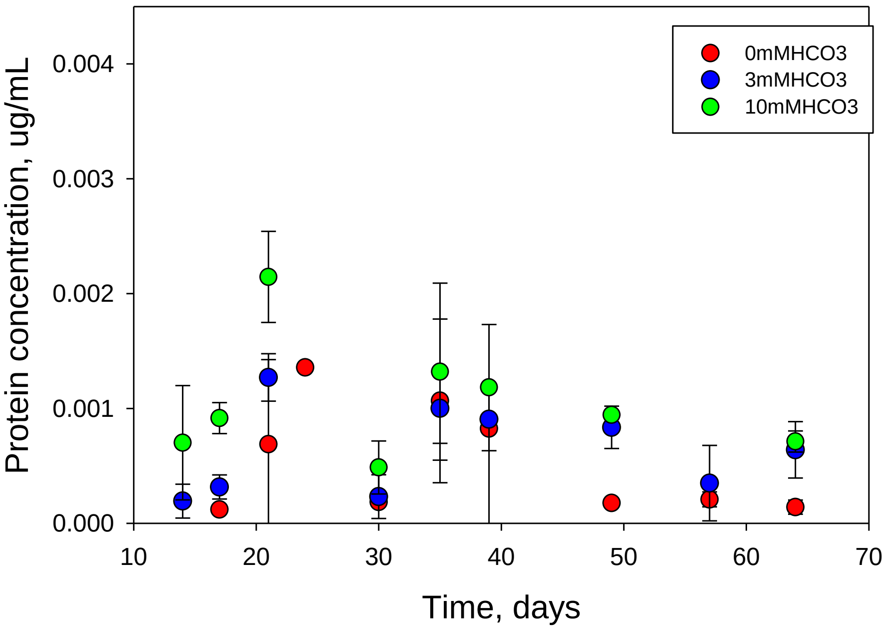


Changes in the direct cell counts for samples containing varying concentrations of bicarbonate

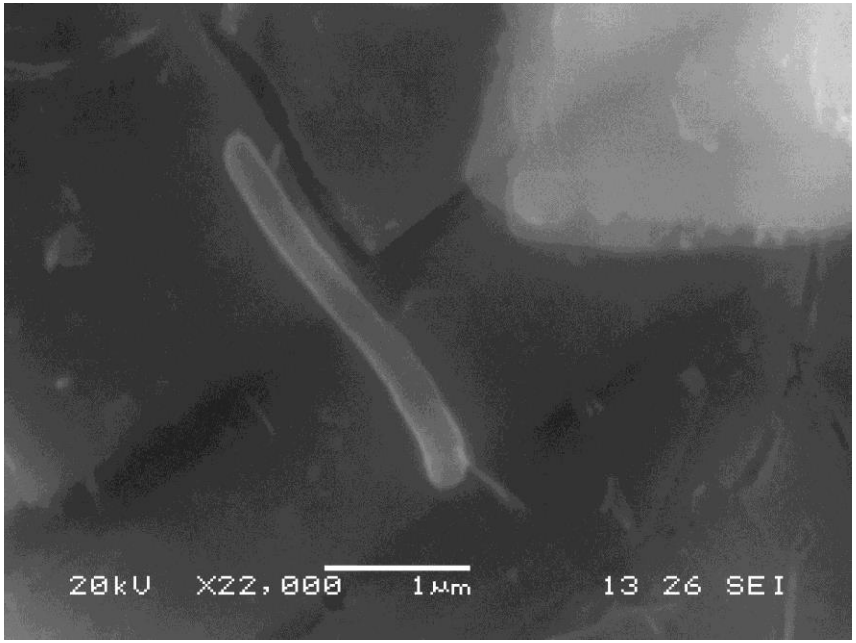
Subtask 1.2: Changes in a Protein Content

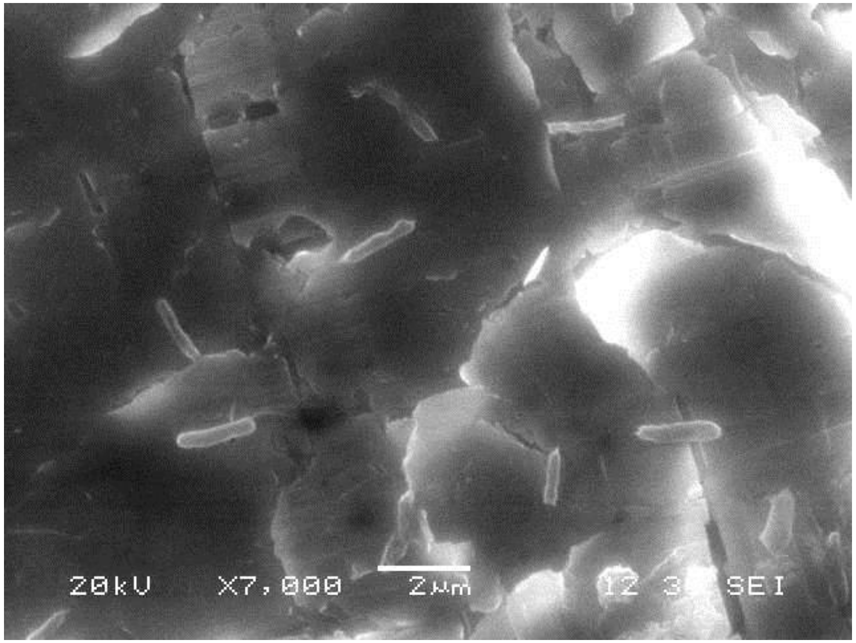
- Linear correlation between cell density of fresh *Shewanella* suspensions and protein content.
- The theoretically calculated total cell density is overestimated compared to the direct visual cell density counting.
  - Exposure to U(VI) might affect the cell physiology resulting in changes of protein masses.

Protein Content vs. Time



Subtask 1.2: SEM Analysis





- Bacteria attachment on the mineral surfaces through specific structures
- No extensive biofilm was observed via SEM.

Subtask 1.2: Speciation Modeling

0 mM HCO_3^-		3 mM HCO_3^-		10 mM HCO_3^-	
Soluble	**Precipitates**	**Soluble**	**Precipitates**	**Soluble**	**Precipitates**
20% UO_2HPO_4	Hydroxylapatite	50% $Ca_2UO_2(CO_3)_3$	Hydroxylapatite	92% $UO_2(CO_3)_3^{-4}$	Hydroxylapatite
80% $UO_2PO_4^-$	Uranyl-phosphate	44% $CaUO_2(CO_3)_3^{-2}$	Uranyl-phosphate	6% $CaUO_2(CO_3)_3^{-2}$	Uranyl-phosphate
	autunite	~6% negatively charged uranyl carbonate complexes	autunite		autunite

- The saturation of hydroxylapatite and uranyl-phosphate phases is predicted in all cases.
- Negatively charged uranyl complexes are less bioavailable due to electrostatic repulsions between negatively charged uranyl complexes and the bacterial cell surface.

Subtask 1.2: Future Experiments

- Replicate the exact conditions (U, Ca and P concentrations along with three different bicarbonate concentrations) in mineral -free experiments.
- Biodissolution of synthetic Na-autunite
- Bacteria consortia for the biodissolution studies

Subtask 1.3: Evaluation of Ammonia and Uranium fate and biological contributions during and after Ammonia injection for Uranium treatment

– Subtask 1.3.1: *Investigation of NH_3 and U partitioning in bicarbonate-bearing media.*

– Subtask 1.3.2 *Bacterial community transformations before and after NH_3 additions.* (Summer PNNL Internship)

– Subtask 1.3.3: *The influence of microbial activity on the corresponding electrical geophysical response after ammonia injections in the vadose zone* (Current Spring PNNL Internship)

Subtask 1.3.1: Investigation of NH3 and U partitioning in bicarbonate-bearing media.

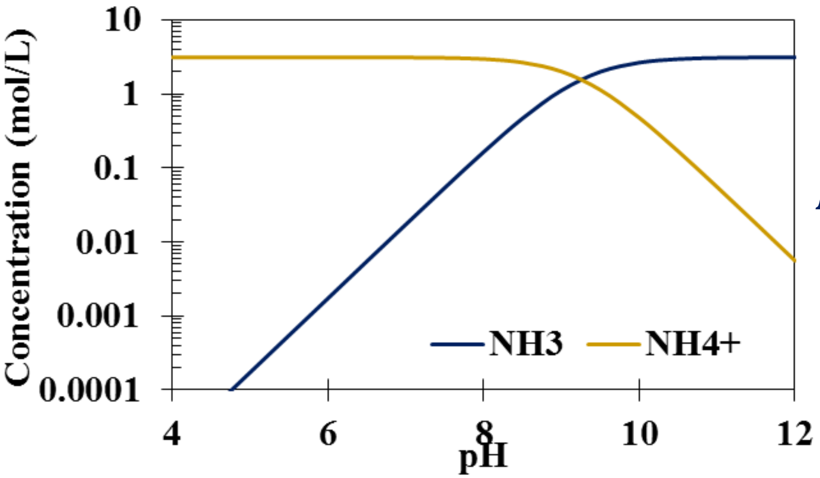
Dr. Hilary Emerson
Silvina DiPietro (DOE Fellow)

FLORIDA INTERNATIONAL UNIVERSITY

Subtask 1.3.1: Background

Ammonia Gas for Remediation

- Additional liquids *cannot* be added to the vadose zone
- Desire to *increase pH* to dissolve natural aluminosilicate minerals and (co)precipitate uranium



Relevant Reactions:

$$NH_{3(aqu)} + H_2O_{(l)} \leftrightarrow NH_4{}^{+}{}_{(aqu)} + OH^{-}{}_{(aqu)}$$

K_a=1.82x10^{-5}

$$NH_{3(aqu)} \leftrightarrow NH_{3(g)}$$

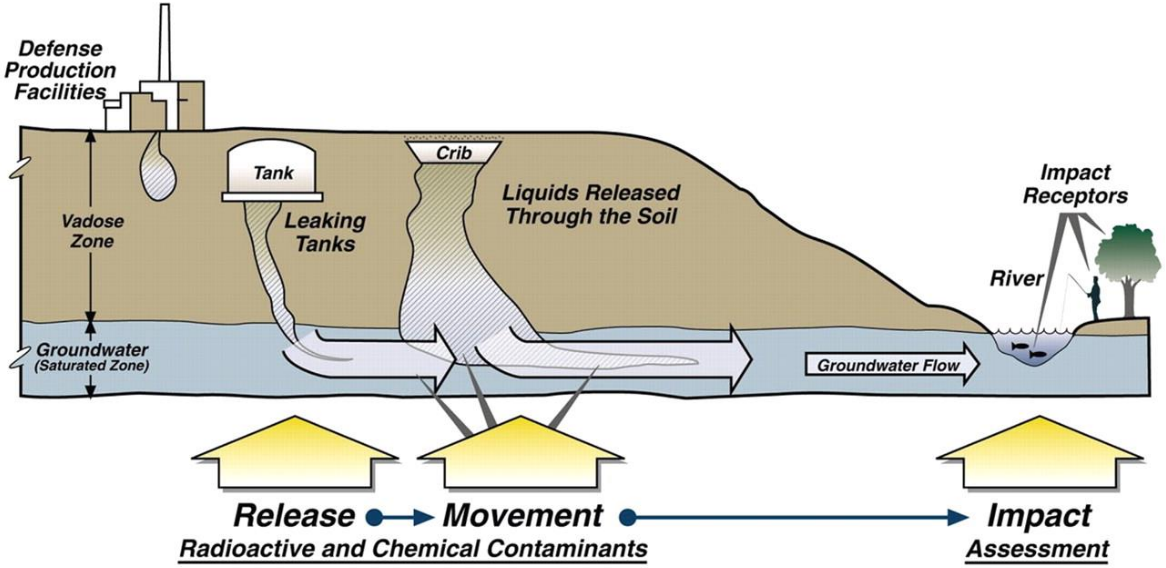
K_H=0.016 atm/mol

Goal: To understand the fate of U and NH_3 gas during and after NH_3 injection into the vadose zone

Subtask 1.3.1

Research Objective

Investigate the effects of ***NH_3 gas*** injection on the ***fate of U and NH_3*** in the presence of pure minerals and Hanford sediments (with a comparison of NaOH vs. NH_3 injection)



Gee *et al.*, 2007

(New task: September 2015 – present)

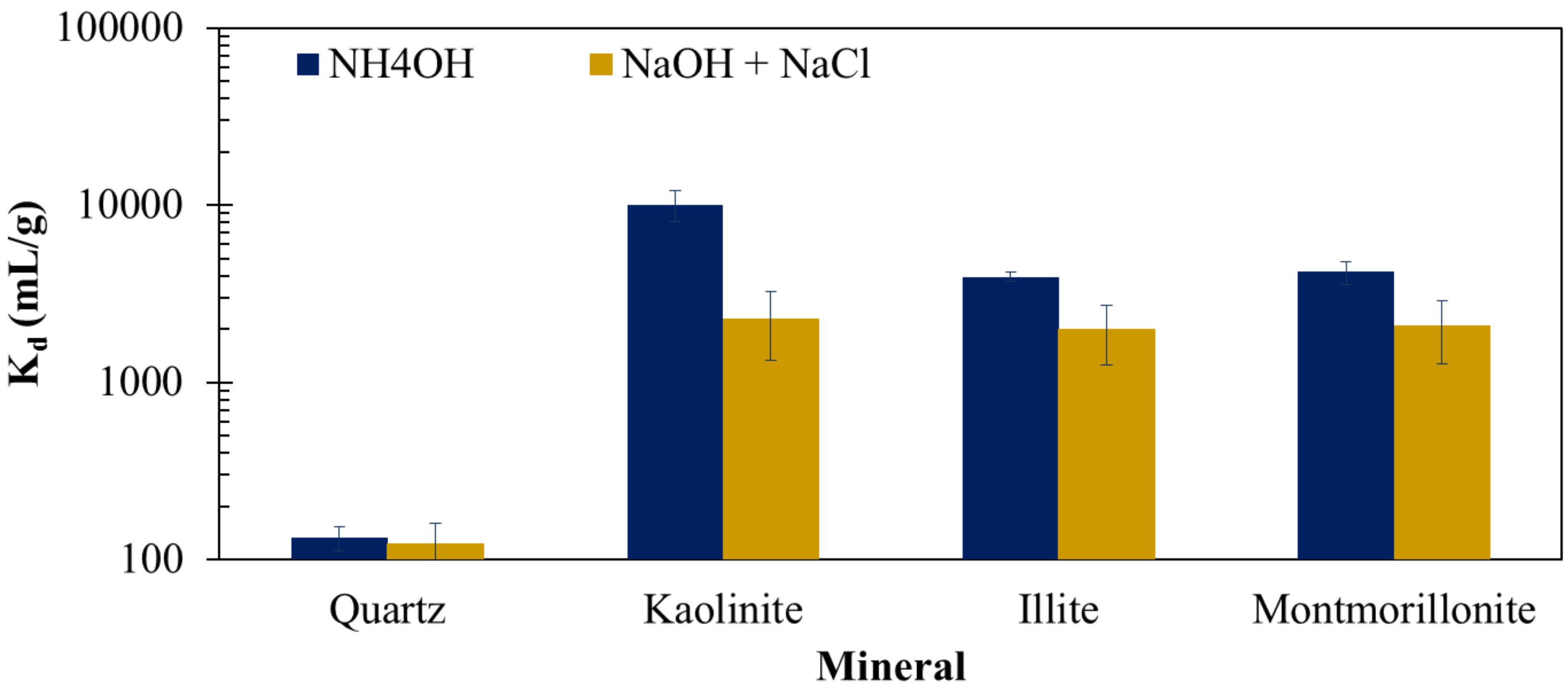
Subtask 1.3.1: NH_3 and U Fate

Experimental Methodology

- Batch experiments:
  1. Natural Conditions: pH ~7.5, ionic strength solution (3.2 mM NaCl or synthetic porewater), mineral (5 g/L – clays or 100 g/L quartz), 500 ppb U(IV)
  2. Following Injection: Adjusted samples in step #1 to pH ~11.5 via 2.5 M NaCl + 0.025 M NaOH or 2.5 M NH_4OH

Subtask 1.3.1: NH_3 and U Fate

Results: Apparent Partitioning Coefficients

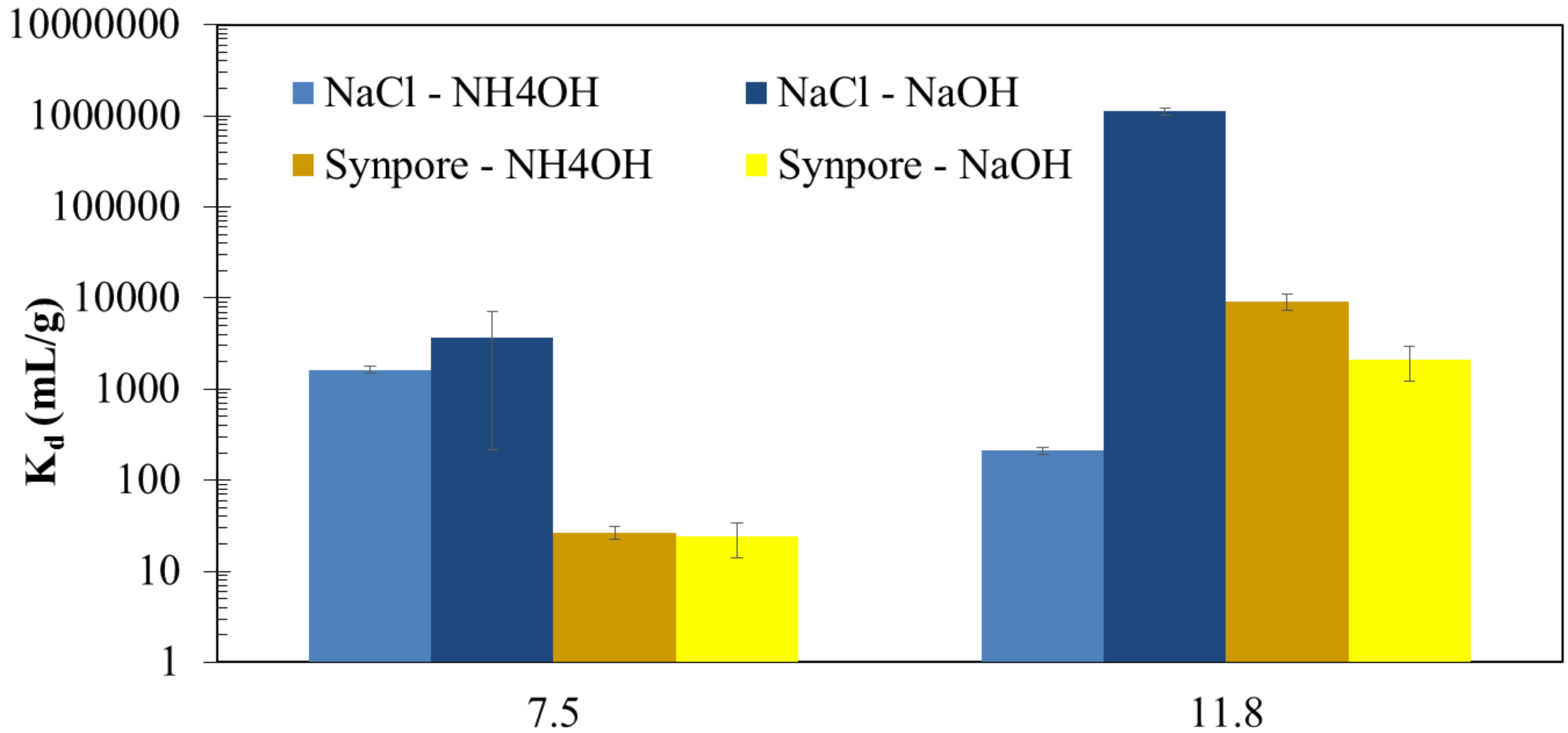


Apparent Kd's – multiple processes are ongoing including sorption, precipitation, and complexation leading to removal of U from the aqueous phase

Note: data is for synthetic porewater

Subtask 1.3.1: NH_3 and U Fate

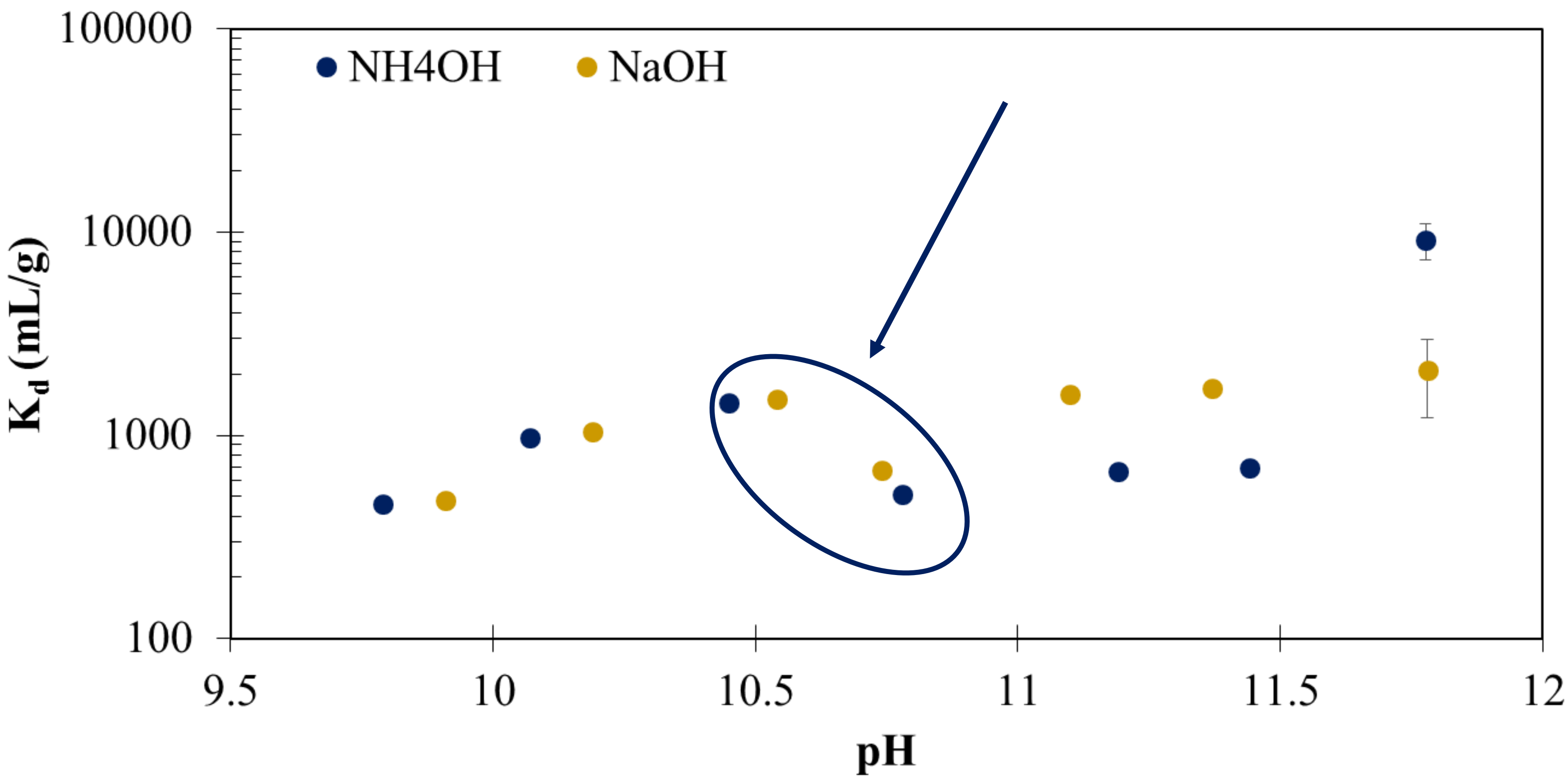
Results: NaCl vs. Synthetic Porewater



Note: data comparison is for Kaolinite, but additional minerals are under investigation

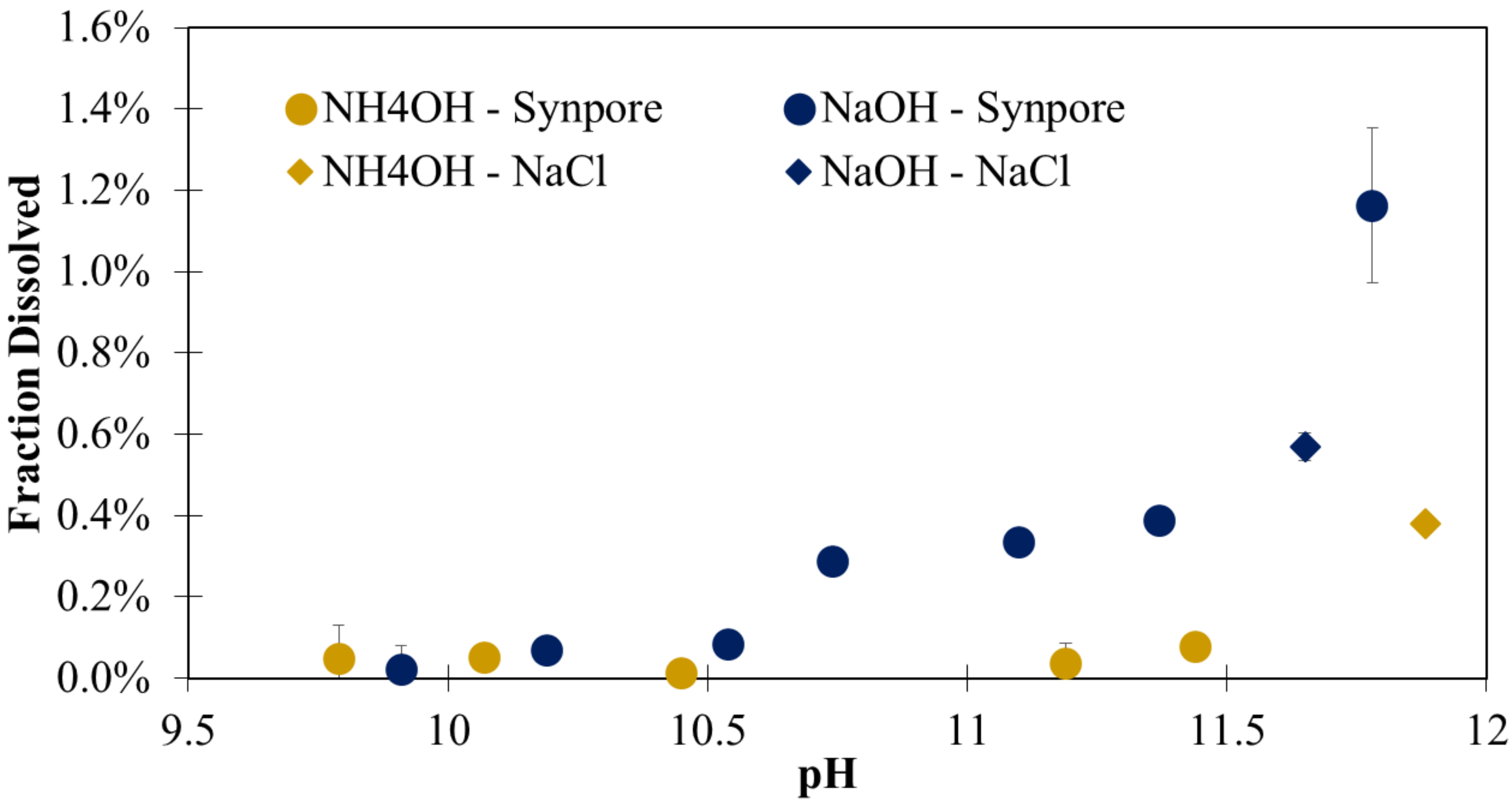
Subtask 1.3.1: NH_3 and U Fate

Results: U Partition vs. pH



Subtask 1.3.1: NH_3 and U Fate

Results: Kaolinite Dissolution



Subtask 1.3.1: NH_3 and U Fate
Discussion

Uranium Fate

- Demonstrated that NH_4OH removes more U from the aqueous phase than NaOH [in the presence of kaolinite, illite and montmorillonite but not quartz].
- Observed a change in U partitioning and mineral dissolution for kaolinite between pH 10.5 and 11 which is likely the point when co-precipitation of U begins to occur.

Mineral Dissolution

- Initial ionic strength does not affect mineral dissolution but does significantly change U partitioning
- NaOH or NH_4OH significantly effect mineral dissolution

Subtask 1.3.1: NH_3 and U Fate

Future Work

- Additional batch experiments with Hanford 200 Area sediments and minerals (calcite and muscovite)
- Sequential extractions to investigate the lability of U following treatments (*ongoing*)
- Speciation modeling and statistical analysis of batch experiments
- Mineral characterization by XRD, BET, SEM-EDS (*ongoing*)

Subtask 1.3.3:The influence of microbial activity on the corresponding electrical geophysical response after ammonia injections in the vadose zone

Alejandro Garcia (DOE Fellow, ARC/FIU)
Under supervision of Dr. Brady Lee (PNNL) and
Dr. Timothy Johnson (PNNL)
Research performed at PNNL

Florida International University

Subtask 1.3.3: Background

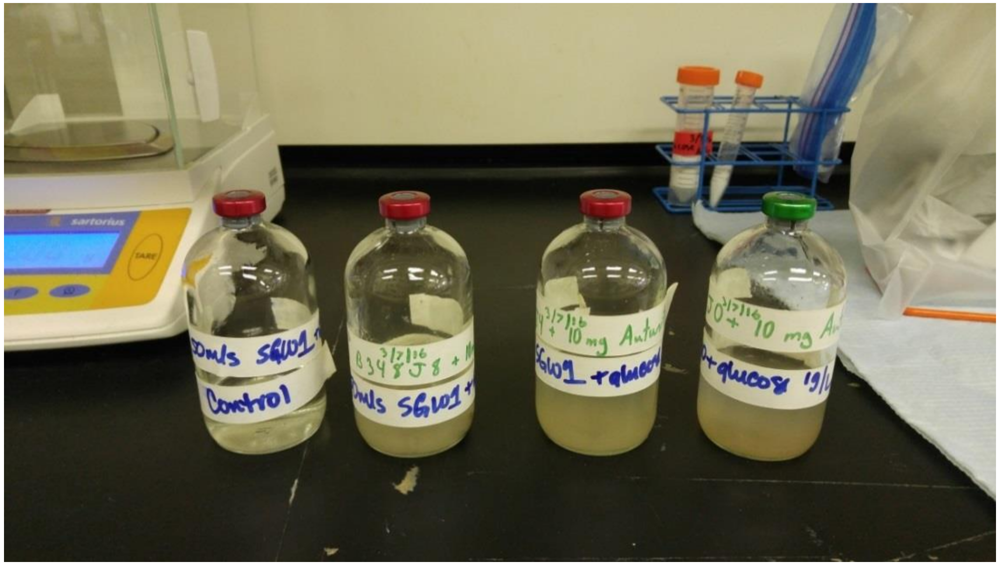
- Goal: to understand the SIP (Spectral Induced Polarization) response to biofilm formation
- Current student internship at PNNL in Spring 2016
- Spectral induced polarization is a geophysical technique, which measures:
  - The impedance between two measuring electrodes due to an injected AC current over various frequencies.
  - SIP responses depend not only on the real conductivity (a measure of charge transport) but also on the imaginary conductivity (a measure of charge storage).
  - It is believed that biofilm formation can produce a measureable change in the imaginary conductivity.

Subtask 1.3.3: Column Design

- Six Columns will be built from a clear pvc pipe with holes drilled on the sides and have large opaque pvc end caps on either end.
- Each column will have:
  - A coiled Ag/AgCl current electrode on either end.
  - 4 potential electrodes equidistant on the side in 4 sample ports,
  - Each electrode will be composed of a silver wire encased in agar gel which is then situated within a pvc nipple.
- Synthetic groundwater injection will occur through bottom inlet with effluent exiting through the top.
- The solution will be pumped at a low flow rate (.10 L/d or less) using a peristaltic pump.
- Each column will have a layer of Hanford sediment mixed with autunite in the center.

Subtask 1.3.3: Internship Update

- Both the pump and the required electrical equipment necessary for SIP measurements have arrived; however, construction of columns is still waiting on some pvc components.
- Microbes are being cultured within a solution composed of synthetic groundwater, Hanford sediment, yeast extract, glucose, and Ca-autunite.



Subtask 1.3.3: Internship Update

- Media solutions were prepared in aerobic conditions within a standard lab hood designated for work with radioactive materials,
  - Cultures were capped and left to sit for ~1-2 weeks before transferring, as such conditions within bottles could be described as oxygen restricted.
- The microbes being cultured are native to the sediment mixed into the solutions.
  - Sediment were collected from clean area at Hanford.
  - The media solution was filter sterilized prior to use in the experiments.
  - The synthetic groundwater used wasn't autoclaved due to precipitation from high heat/pressure.

Subtask 1.3.3: Future work

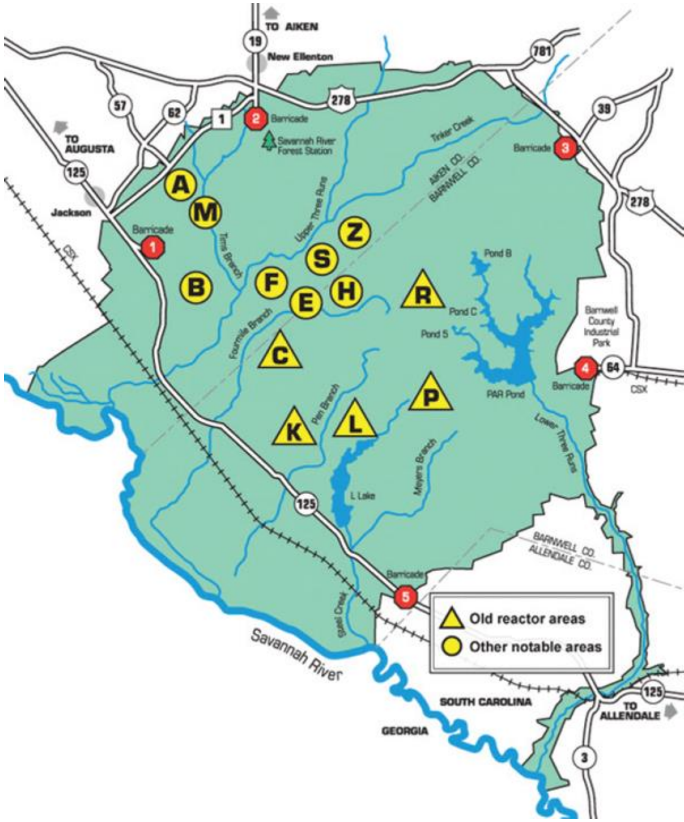
- Complete with the experimental set up.
- Initiate experimental work at FIU

Task 2:
Remediation Research and Technical Support for Savannah River Site

FLORIDA INTERNATIONAL UNIVERSITY

Task 2: Background

- The Savannah River Site (SRS) was one of the most significant sites for the production of materials related to the U.S. nuclear program during the early 1950s to late 1980s.
- An estimated 36 metric tons of plutonium were produced, and 3.4 billion gallons of hazardous waste solution were received in the F and H areas.
- The constituents of concern (COCs) associated with the F and H Area HWMF groundwater plume are uranium-238, tritium, iodine-129, strontium-90, curium-244, americium-241, technetium-99, cadmium, and aluminum, and mercury.



Subtask 2.1 FIU's Support for Groundwater Remediation at SRS F/H Area

Dr. Vasileios Anagnostopoulos
Alejandro Hernandez DOE Fellow)
Christine Wipfli (DOE Fellow)

Florida International University

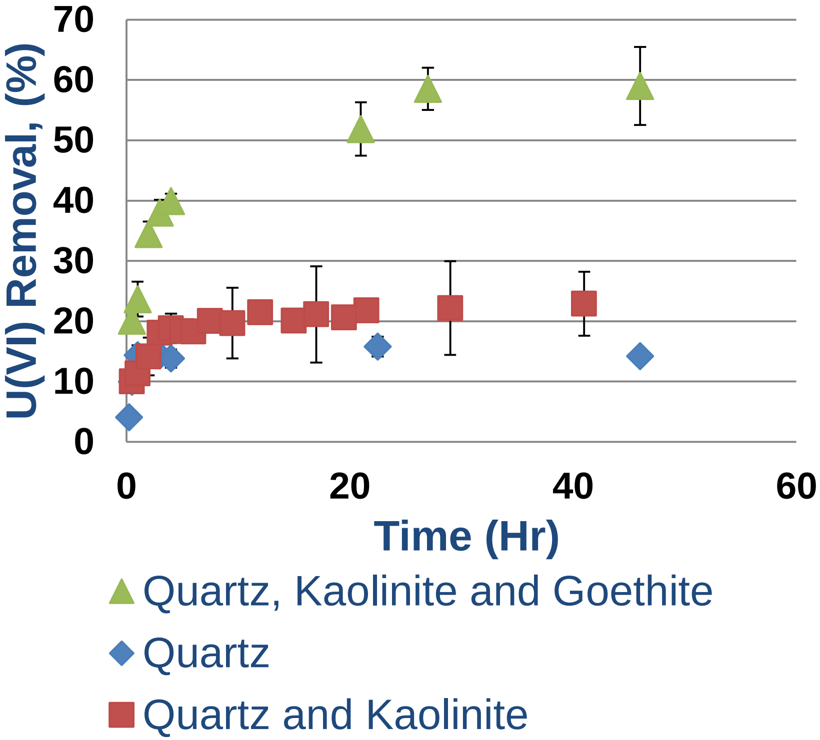
Subtask 2.1: Objectives

1. Explore the application of sodium silicate for the restoration of the alkalinity of the treatment zone.
2. Investigate the immobilization of COCs, concentrating on U(VI).
3. Elucidate the sorption properties of U(VI) on SRS soil at circumneutral conditions, through kinetic and mechanistic studies.

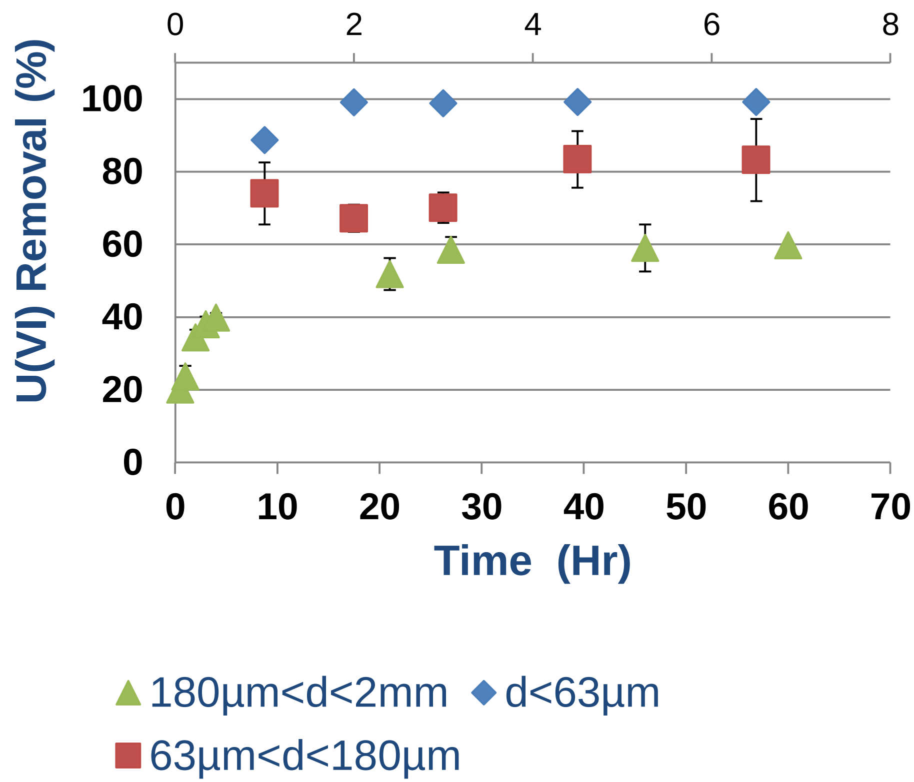
Subtask 2.1: Results on Sorption Kinetics

FIU Applied Research Center

Kinetics of U(VI) Sorption on Different Mineral Phases



Kinetics of U(VI) Sorption on Different SRS Soil Fraction



Subtask 2.1: Results on Sorption Kinetics

- Sorption kinetics experiments were preformed with mixtures of synthetic minerals, to mimic the SRS soil composition
- U(VI) removal in the presence of quartz and kaolinite was found to be only 23%, when 95% quartz and 5%kaolinite mixture was used
- In the presence of quartz, kaolinite and goethite (actual SRS soil) almost 60% of the U(VI) in the aqueous phase has been removed
- SRS soil was sieved to obtained different SRS soil fractions: d<63 μm, 63μm<d<180μm, and 180μm<d<2mm
- A trend was observed: the smaller the average particle diameter, the higher the U(VI) removal

Subtask 2.1: SEM/EDS Analysis

Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy or SEM/EDS

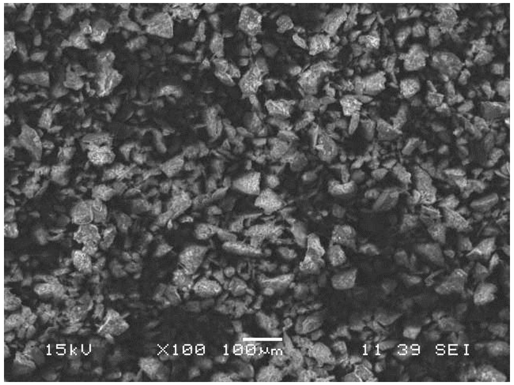


Figure 1. SRS Soil Fraction: d<63 µm

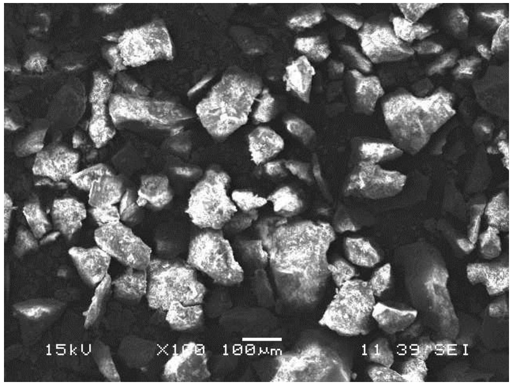


Figure 2. SRS Soil Fraction: 63µm<d<180µm

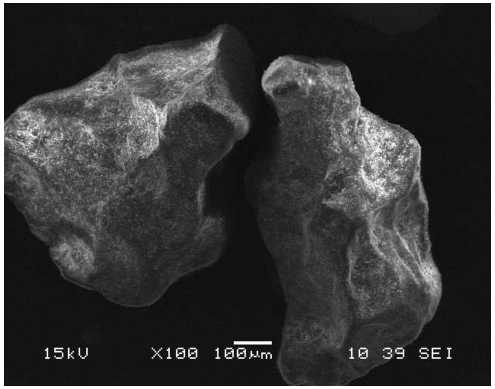


Figure 3. SRS Soil Fraction: 180µm<d<2mm

SRS Soil Fraction	U(VI) % Removed	[Fe] (mg/g)	[Al] (mg/g)	[Si] (mg/g)
d<63µm	99±0.2	89±2	72±4	396±3
63µm<d<180µm	79±8	70±11	71±5	389±4
180µm<d<2mm	59±1	40±4	54±13	416±37

Subtask 2.1: Conclusions

- Quartz and kaolinite concentrations remain at the same levels throughout the different fractions;
- The concentration of iron clearly increases with the decrease of average particle diameter;
- U(VI) removal increases as the average particle diameter decreases;
- Possible reasons contributing to higher U(VI) % removal: the higher Fe content and the increase of surface area.
- Goethite is the most reactive mineral phase in the SRS soil.

Subtask 2.1: Future Work

- Desorption experiments for the finer SRS fractions
  - to compliment with the existing results of desorption on bulk SRS soil fraction, as well as synthetic mineral mixtures.

- Experimentally determine the surface area of the different SRS soil fractions.
- Design experiments to clarify whether the higher Fe content or the surface area increase plays a pivotal role on U(VI) removal.
- Evaluate the results of BCR sequential extraction experiments.

Subtask 2.2. Monitoring of U(VI) Bioreduction after ARCADIS Demonstration at the SRS F-Area

Dr. Yelena Katsenovich
Aref Shehadeh (DOE Fellow)

Florida International University

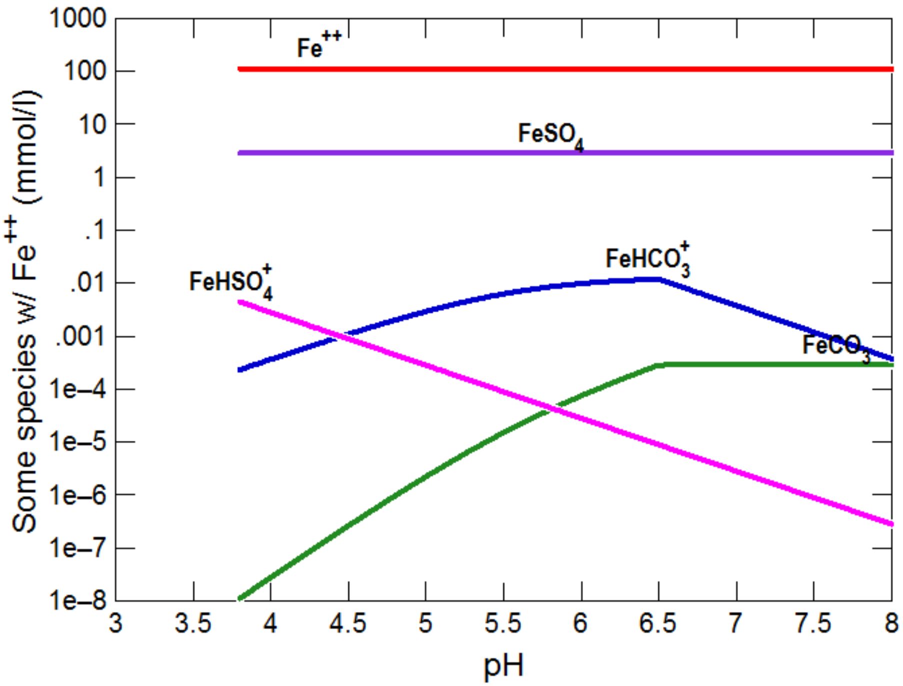
Subtask 2.2: Objectives

- Evaluation of microcosms mimicking the enhanced anaerobic reductive precipitation (EARP) remediation method previously tested at SRS F/H Area.
- The addition of the molasses to GW produces anaerobic conditions conducive to the reductive precipitation of uranium,
  - less soluble in +4 oxidation state.
- Determine the range of environmental conditions in which the formation of siderite and pyrite solid phases would occur.
- This would extend knowledge and improve understanding on the applicability of this technology.

Subtask 2.2: Speciation Modeling

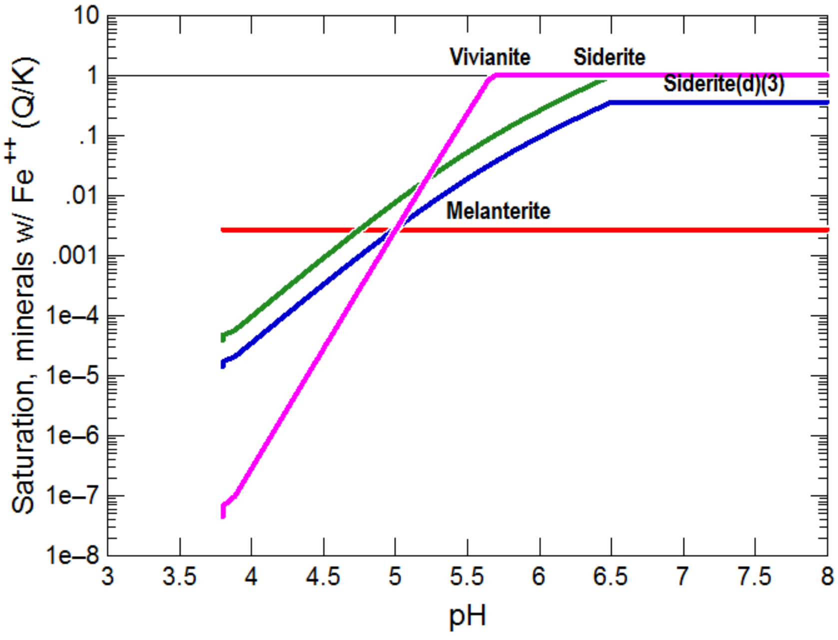
FIU Applied Research Center

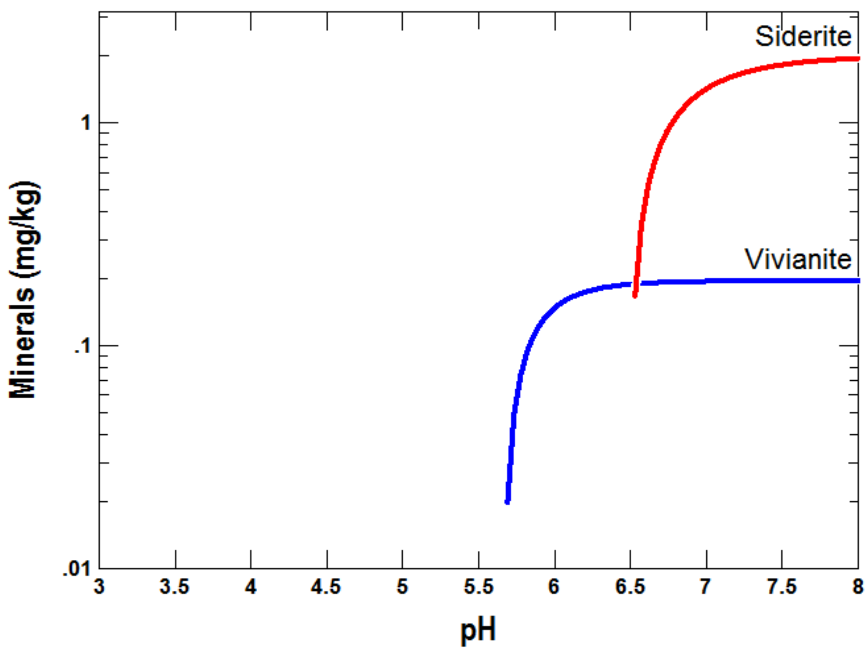
Aqueous species



- pH reduced to ~4 due to molasses fermentation;
- Iron concentration increased to 7-12 mg/L
- The concentration of the initially added sulfate of 500ppm didn't change;
  - No sulfate reduction.

Subtask 2.2.: Speciation Modeling





Speciation modeling via GWB. The formation of siderite is observed at pH ~7. The concentration and weight % of siderite is very small.

Subtask 2.2: Conclusions

- No pyrite solid phases formation;
- Siderite forms only at neutral conditions;
- At acidic pH, ferrous iron will be easily flushed out from the treatment zone
  - No formation of reduced iron solid phases.
- Write a scientific paper on results of these experiments;
- This subtask will not be continued next year.

Subtask 2.3: The Sorption Properties of Humate Injected into the Subsurface

Hansell Gonzalez (DOE Fellow)
Dr. Vasileios Anagnostopoulos
Dr. Yelena Katsenovich

Florida International University

Subtask 2.3:Background

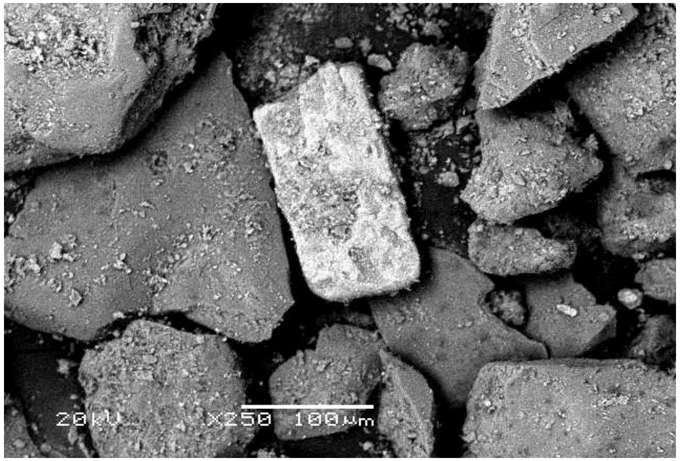
FIU Applied Research Center

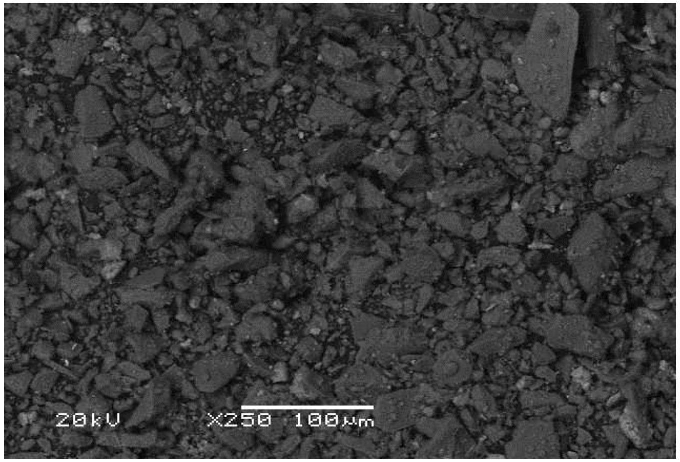
- Huma-K is a soil amendment sold by Land and Sea Organics.
- Huma-K comes from the alkaline extraction of Leonardite (a low-rank coal).
- It contains a minimum of 86% of humic acid

Subtask 2.3: Objectives

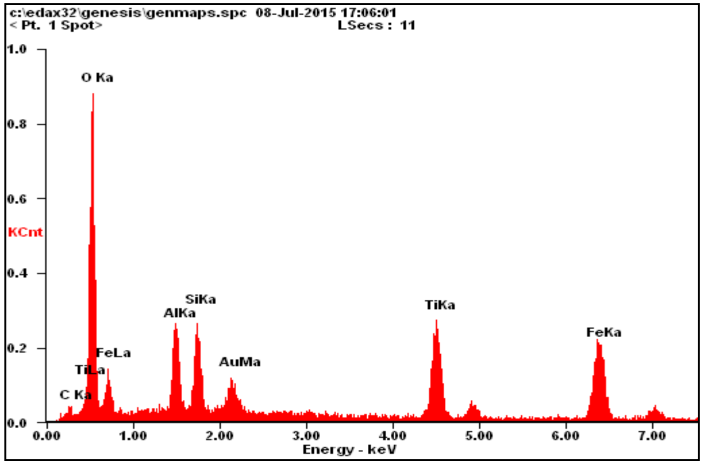
- The principal objective of this study is to determine if the low cost unrefined humate solution known as Huma-K can be used to facilitate uranium adsorption to control the mobility of uranium in acidic groundwater.
- This objective will be fulfilled by completing the following specific aims:
  1. Characterization of Savannah River Site sediments and Huma-K.
  2. Sorption behavior of Huma-K on Savannah River Site sediments.
  3. Removal of Uranium using Huma-K coated sediments.

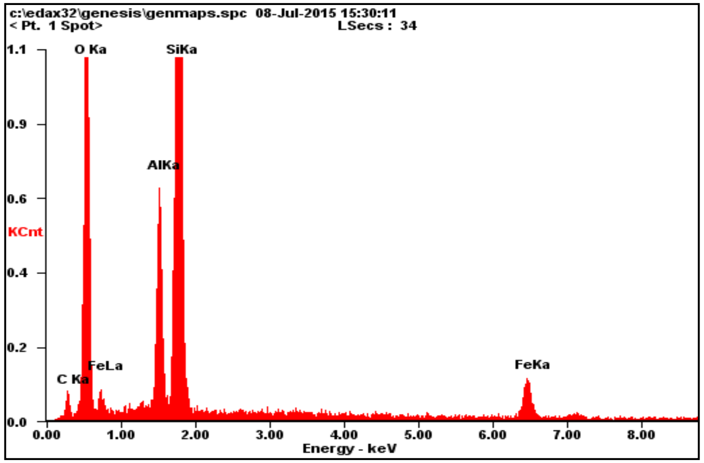
Subtask 2.3: SEM/EDS Results





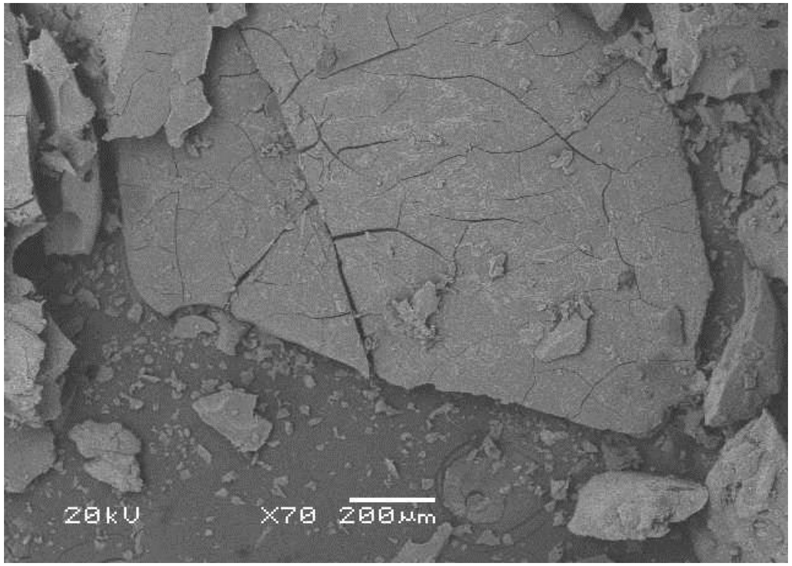
SEM of SRS Sediments coarse fraction (left image) and fine fraction (right image)

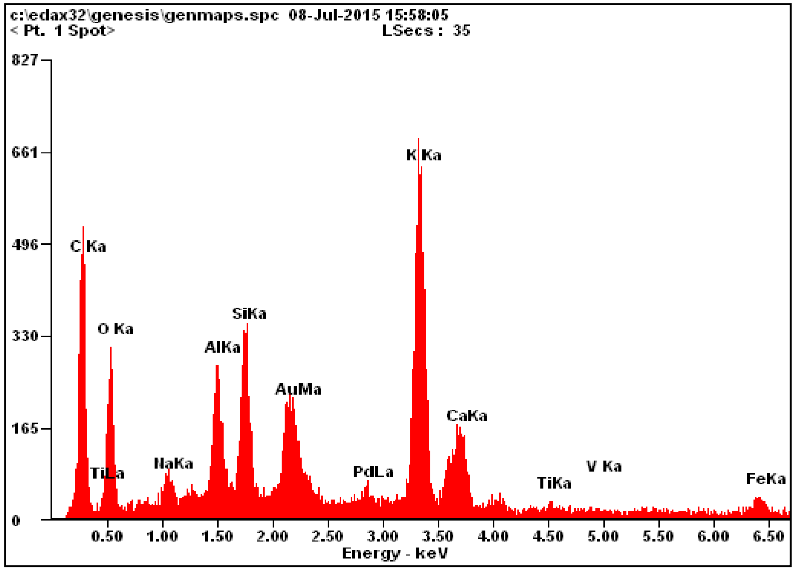




EDS results of SRS Sediments coarse fraction (left image) and fine fraction (right image)

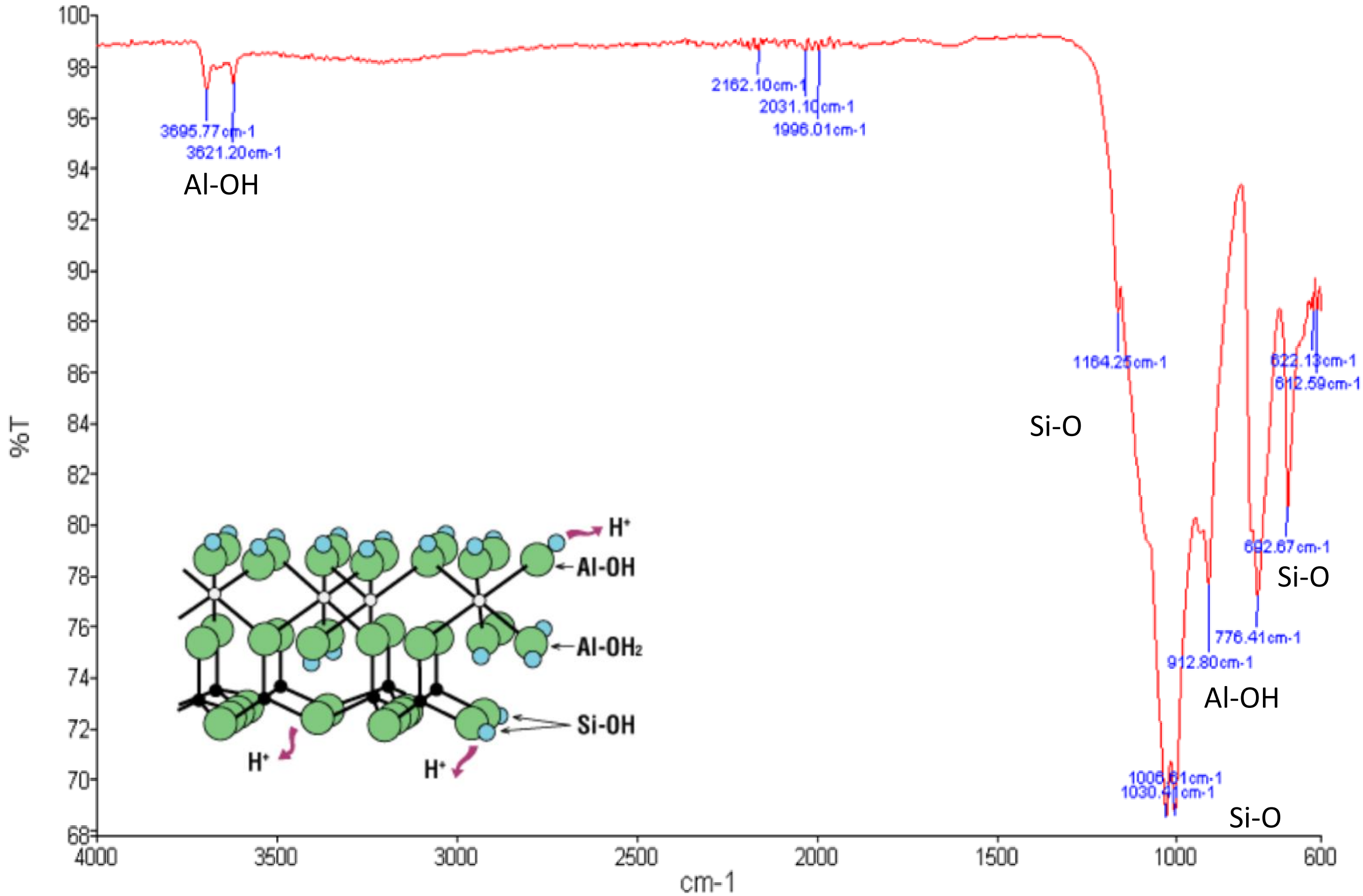
Subtask 2.3: SEM/EDS Results





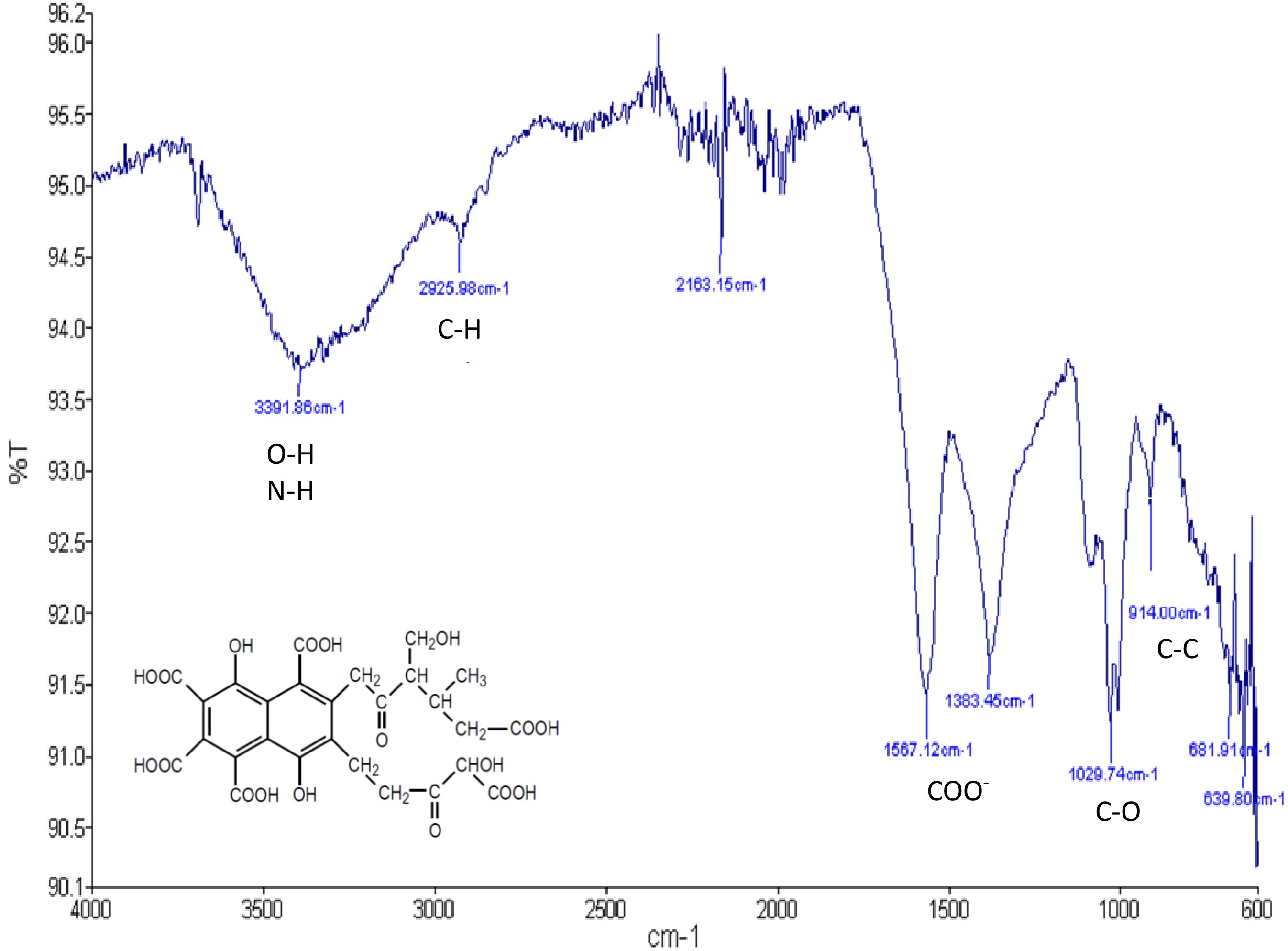
SEM of Huma-K (left image) and EDS analysis (right image)

Subtask 2.3: FTIR Analysis



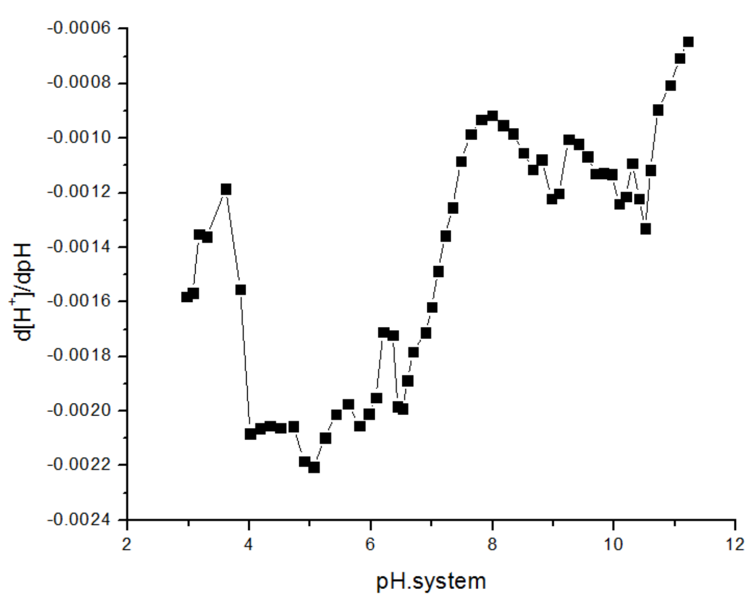
FTIR of SRS Sediments (fine fraction)

Subtask 2.3: FTIR Analysis

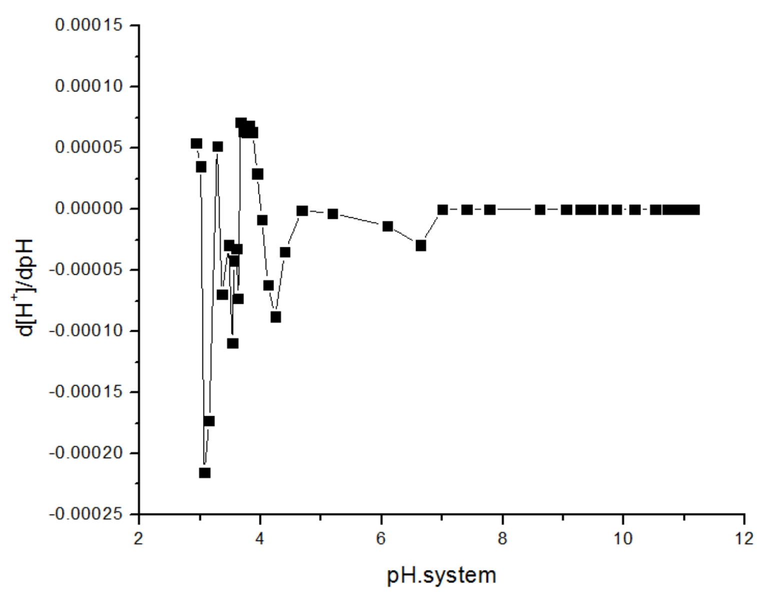


FTIR of Huma-K

Subtask 2.3: Potentiometric Titration



Potentiometric Titration of Huma-K



Potentiometric Titration of SRS sediments

Subtask 2.3: Conclusions

- EDS analysis, FTIR, and potentiometric titrations verify presence of humic substances in Huma-K.
- EDS and FTIR confirm the presence of kaolinite in the fine fraction of SRS sediments. Potentiometric titrations indicate that sediments have similar acido-basic properties as quartz mineral.

Future Work

- First manuscript for publication will include the experimental work investigating HumaK as a low-cost remediation method for acidic groundwater contaminated with uranium.
- Kinetics experiment for sorption of Uranium on Savannah River Site sediments with and without Huma-K.

Subtask 2.4: The Synergetic Effect of HA and Si on the Removal of U(VI)

Dr. Ravi Gudavalli
Alexis Smoot (DOE Fellow)
Christian Pino(DOE Fellow)

Florida International University

Subtask 2.4: The Synergetic effect of HA and Si on the removal of U(VI)

Background:

- F/H area seepage basins received acidic waste containing radionuclides such as uranium.
- Humic acid carries a large number of functional groups, acts as an important scavenger in ion exchange and as a metal complexing ligand.

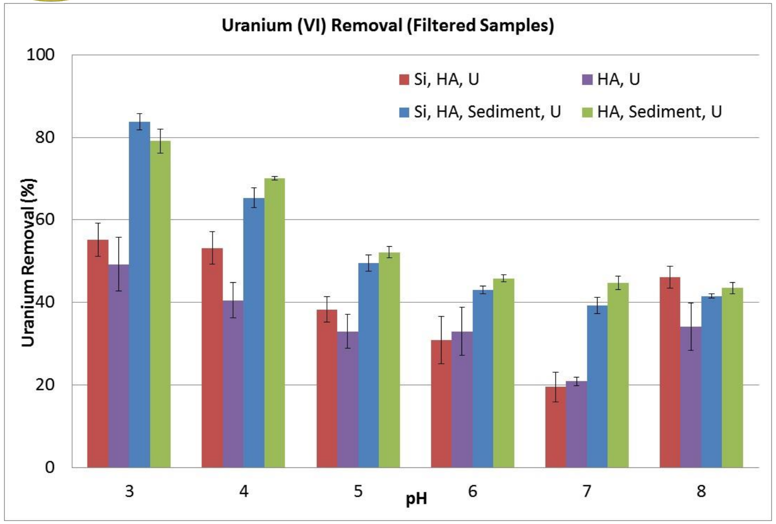
Objectives:

- Investigate synergetic interactions between humic acid (HA) and colloidal silica that may influence the removal of uranium in the presence of SRS sediments
- Evaluate the effect of 30 ppm of HA and compare results with previously obtained data on the addition of 10 and 50 ppm of HA

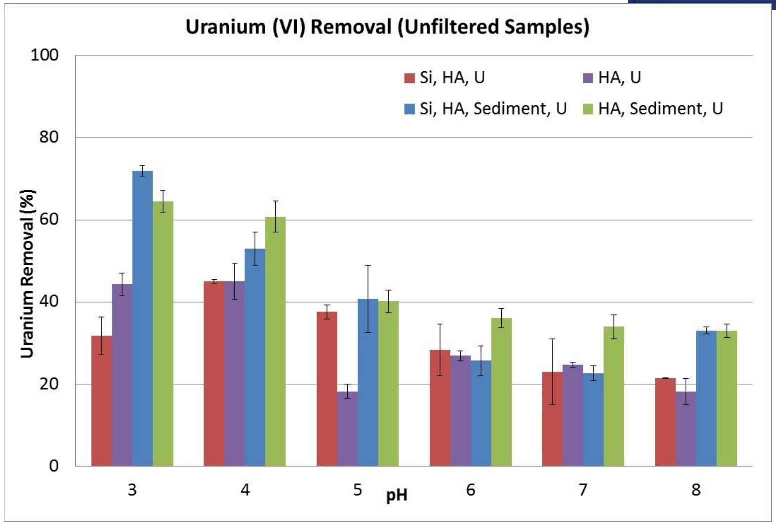
Subtask 2.4: Methodology of Experiments

- Multi-component batch systems with a pH range from 3 to 8 were constructed to effectively analyze each of these parameters and their synergistic contributions to the removal of U(VI) from the aqueous phase.
    - Batch 2: Si (3.5 mM) + U(VI) (0.5 ppm) + HA (50 ppm), (no sediments)
    - Batch 3: U(VI) (0.5 ppm) + HA (50 ppm), (no Si or sediments)
    - Batch 5: Sediments + Si (3.5 mM) +U (VI) (0.5 ppm) + HA (50 ppm)
    - Batch 6: Sediments + U(VI) (0.5 ppm) + HA (50 ppm), (no Si)
- Samples were placed on platform shaker for 2 days
    - After two days, samples were centrifuged
    - Filtered and unfiltered samples were analyzed via KPA and ICP

Subtask 2.4: Results



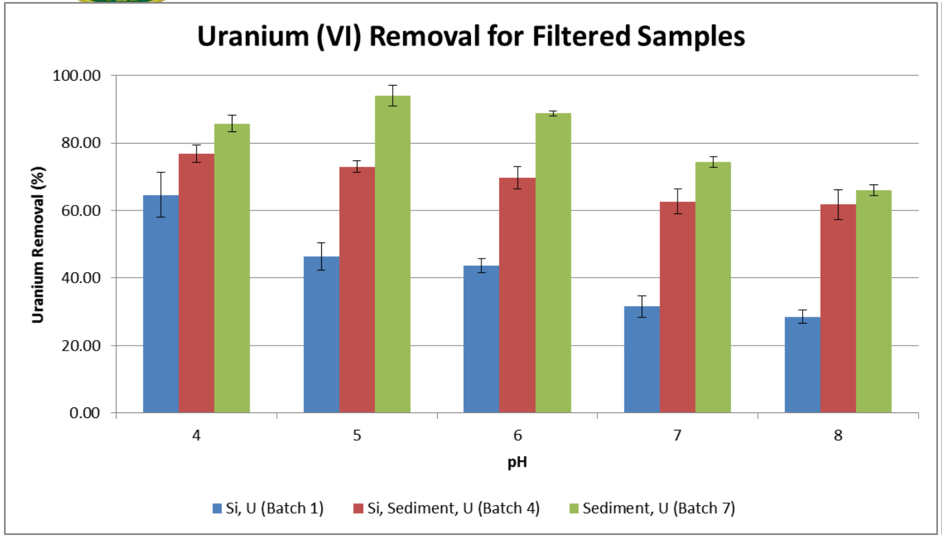
Uranium (VI) Removal Filtered between pH 3 and 8

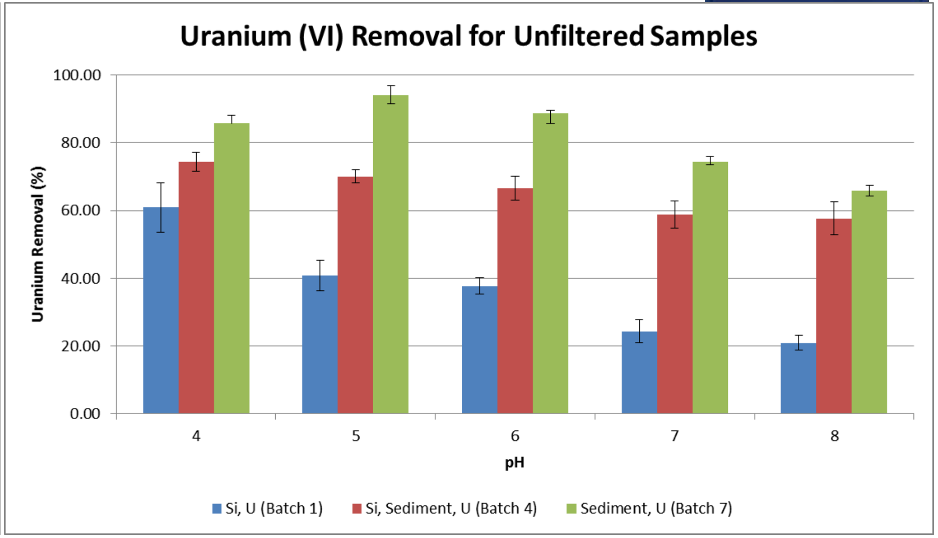


Uranium (VI) Removal Unfiltered between pH 3 and 8

- The percent removal of uranium is directly influenced by the presence and interactions of humic acid and sediment.
- The sediment included in the samples was revealed to increase the percent removal of uranium at all pHs relative to non-sediment-bearing batches.
- Uranium removal at pH 3 yielded a 35% increase in the presence of sediment; as the pH reaches near neutral, the effectiveness of sediment at increasing uranium removal diminishes to 8%.

Subtask 2.4: Results





- Prepared batch with a pH range from 3 to 8 for samples containing no HA
  - Batch 1: Si (3.5 mM) + U(VI) (0.5 ppm)
  - Batch 4: Si (3.5 mM) + U(VI) (0.5 ppm) + sediments
  - Batch 7: Sediment + U(VI) (0.5 ppm)
- Batch 1 and Batch 4 showed a decreasing trend in uranium removal, addition of sediment increased uranium removal
- Batch 7 had a maximum removal at pH 5 (93.98%) then decreased to 65.93% at pH 8

Subtask 2.4: Results

- Initiated synergy experiments with 30 ppm of humic acid
  - Completed two sets of experiments with pH 3 and 4 samples
  - pH of the samples was measured daily and adjusted if different
  - Samples will be analyzed and data will be reported

Subtask 2.4: Future Work

- Complete experiments, pH 5-8
- Compare data with previous experiments
- Repeat any necessary experiments

Subtask 2.5: Investigation of the migration and distribution of natural organic matter injected into subsurface systems

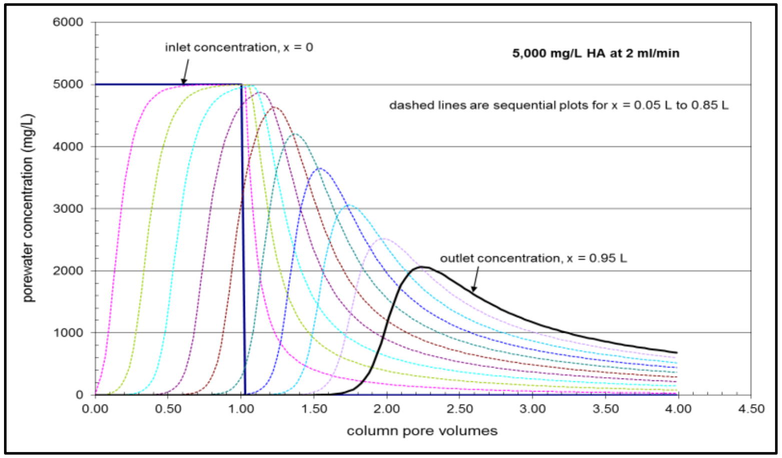
Dr. Ravi Gudavalli
Kiara Pazan(DOE Fellow)
Sarah Bird (DOE Fellow)

Florida International University

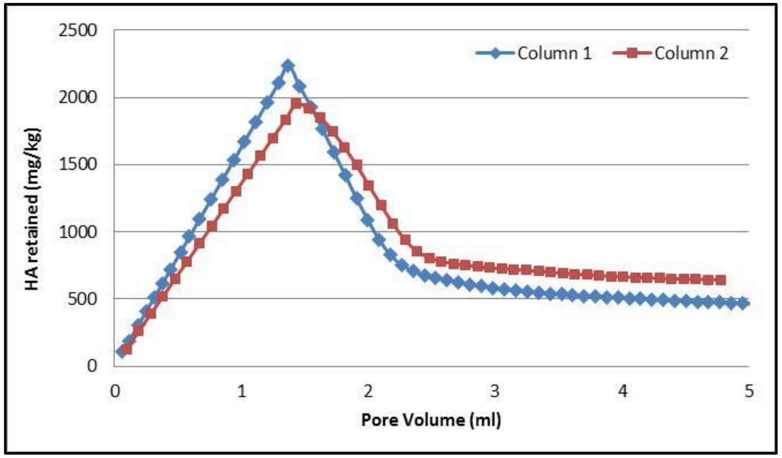
Subtask 2.5: Objectives

- To evaluate the potential use of Huma-K to enhance attenuation of uranium in the acidic F-Area aquifer.
- To study the migration and distribution of Huma-K injected into subsurface systems via column experiments.
- To obtain sorption and desorption parameters under different pH levels.
- To study the effect of HA on uranium mobility through porous media via flow-through column experiments.

Subtask 2.5: Accomplishments



Simulated Huma-K injection scenario



Huma-K retention during column studies

- 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.

Subtask 2.5: Accomplishments

FIU Applied Research Center

- Column 1 was drained and soil was divided into 6 sections and a small amount of each section was oven dried at 35°C for 2-days.

- A representative sample from each section was used to perform SEM-EDS analysis.
  - Analysis revealed that the concentration of carbon in the sample increased as it moved in the direction of flow.

- One sample was taken from the homogeneous mixture of soil used in the column and was used for SEM analysis.

- Column 2 was drained and samples were prepared in similar fashion for SEM-EDS analysis.

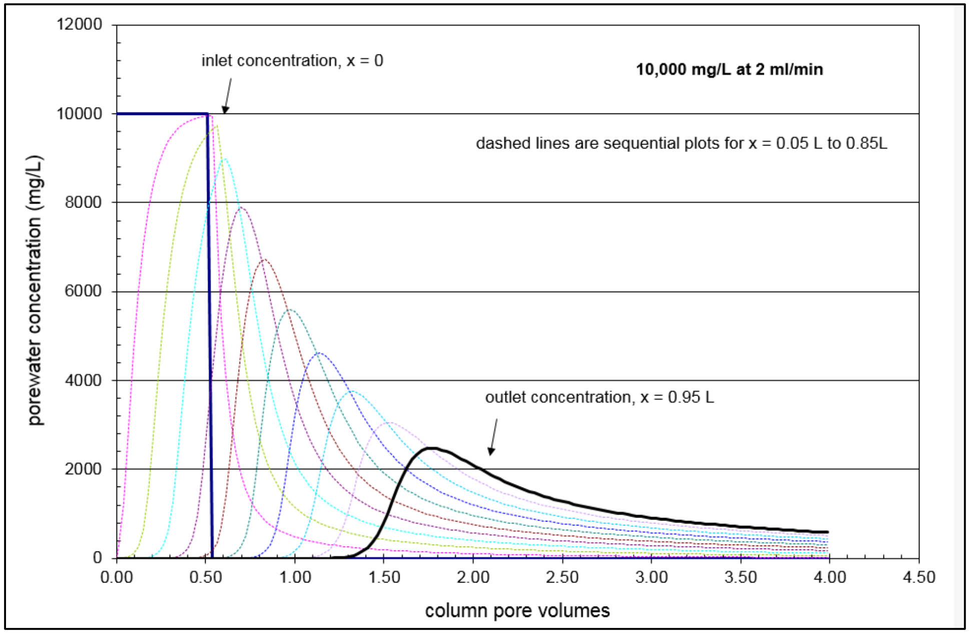
Subtask 2.5: Accomplishments

FIU Applied Research Center

- Soil from representative sections of the columns similar to that used in SEM was oven dried and ground to obtain fine particles for TOC analysis.
  - Samples were sent to FIU's Southeast Environmental Research Center (SERC) for TOC analysis to get quantitative data of humic acid retained in the columns.
  - 10 mg of fine soil sample was used to measure TOC in the samples, sample concentration was below detection limit.
  - Analysis will be repeated with 40 mg of sample to overcome detection limit.

Subtask 2.5: Accomplishments

- Updated the test plan based on discussions with SRS collaborators to optimize the experiments.
- Updated simulations to optimize humic acid injections for only 0.5 PV of humic acid as opposed to 1.0 PV of humic acid previously used
  - Based on the data obtained and discussion with SRS collaborators, 10,000 mg/l and 2 ml/min flow rate was chosen.



Subtask 2.5: Future Work (FIU Performance Year 6)

FIU Applied Research Center

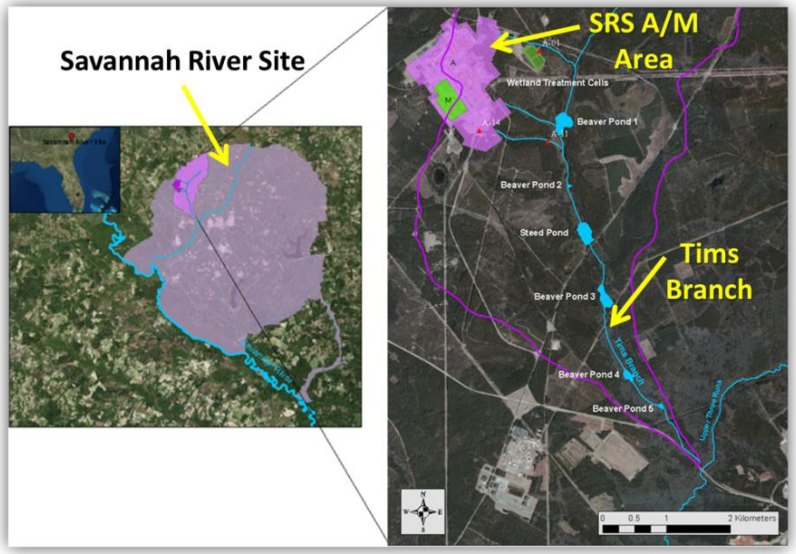
- Complete column experiments by injecting 0.5 PV of humic acid, study the sorption/desorption of humic acid.
- Inject uranium through the column and study the effect of sorbed humic acid on uranium mobility.
- Analyze data and prepare draft report on the results.

Task 3: Surface Water Modeling of Tims Branch

Florida International University

Task 3: Background

- Tims Branch watershed (TBW) impacted by 60 yrs of discharges from SRS process and laboratory facilities.
- Tin introduced into TBW during application of a mercury (Hg) remediation technology, which involved injection of stannous (tin) chloride into Hg-contaminated groundwater.
- Understanding the fate and transport of tin and its compounds is of primary importance due to potential tin methylation where environmental conditions are favorable. Methylated tin is of great environmental concern due to its toxicity to humans and animals.



- Although precipitated tin is primarily deposited as sediment, remobilization may occur during episodic extreme events, such as storms or heavy rainfall, where sediment can be resuspended in the water column and deposited further downstream.

Task 3: Objectives

Objectives:

Application of GIS & stream/ecosystem modeling tools to examine the response of Tims Branch to historical discharges and DOE-EM's remediation actions. This involves:

- Development of an integrated hydrological model of TBW (Subtask 3.1).
- Development of a GIS-based data management system (geodatabase) and the use of GIS tools for processing and visualization of spatial and temporal data to support hydrological model development (Subtask 3.2).
- Sample and data collection for development of an eco-hydrological database to support the modeling efforts. Student support for sample and data collection is anticipated during student internships in collaboration with SRNL/SREL (Subtask 3.3).

Subtask 3.1: Modeling of surface water and sediment transport in the Tims Branch ecosystem

Dr. Noosha Mahmoudi
Dr. Shimelis Setegn
Natalia Duque (DOE Fellow)
Christopher Strand (DOE Fellow)

Florida International University

Subtask 3.1: Description

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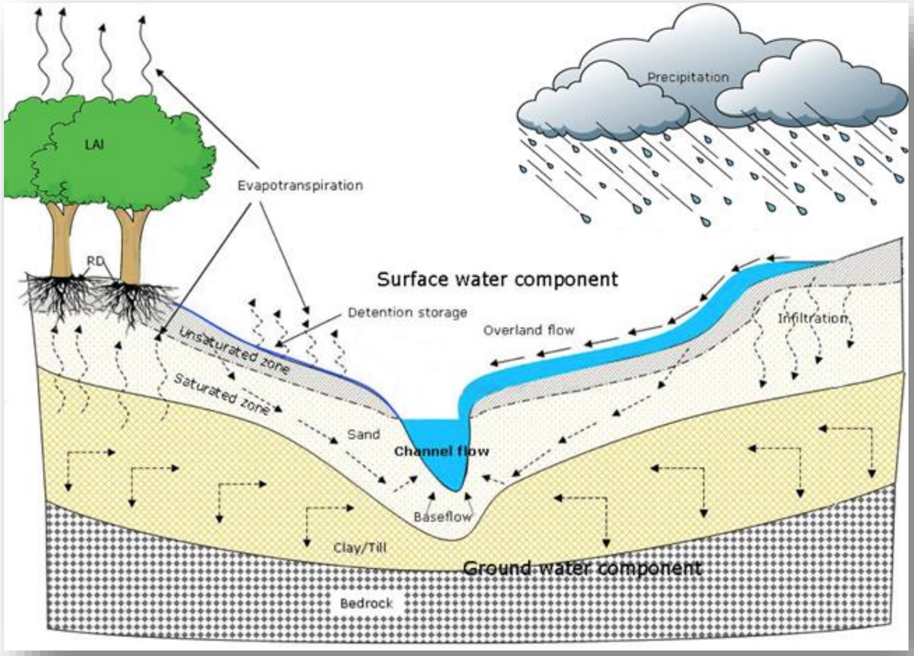
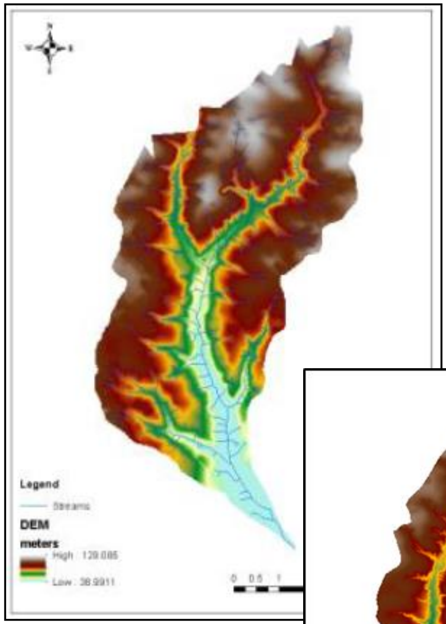
- Aim is to develop an integrated surface/subsurface flow & contaminant transport model of TBW.
- Conceptualizes hydrology and transport mechanisms.
- Simulates surface water flow velocity, depth, and discharge over time in TBW.
- Estimates spatiotemporal distribution of various contaminant concentrations such as tin and mercury in TBW.
- Predicts fate and transport of contaminants in surface water under different environmental and atmospheric conditions.

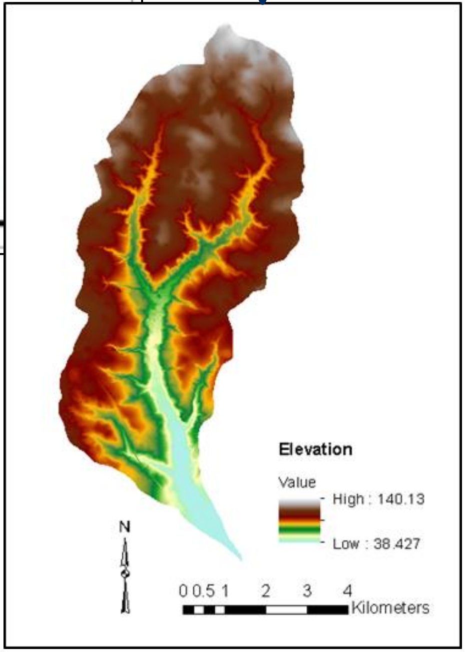


Subtask 3.1: Accomplishments

- Data review and collection of input parameters to set up MIKE SHE model.
- Topographic data modification based on a revised model domain of TBW.
- **Overland Flow** module developed:
  - Uses historical precipitation, groundwater levels, geological data, and river discharges retrieved from government databases.
  - Modified MIKE SHE configuration parameters for simulation of overland flow for revised model domain.
  - Map of Manning's roughness coefficient values generated.
  - Detention Storage value, and Surface-Subsurface Leakage Coefficients assigned (based on literature).
  - Separated Flow Areas assigned as domain area.
  - Simulates surface hydrology throughout TBW.
  - Simulates spatiotemporal distribution of flow discharges, flow duration, and water levels in TBW.



Previous model domain included portion of TBW within SRS boundary.



Revised model domain includes entire TBW.

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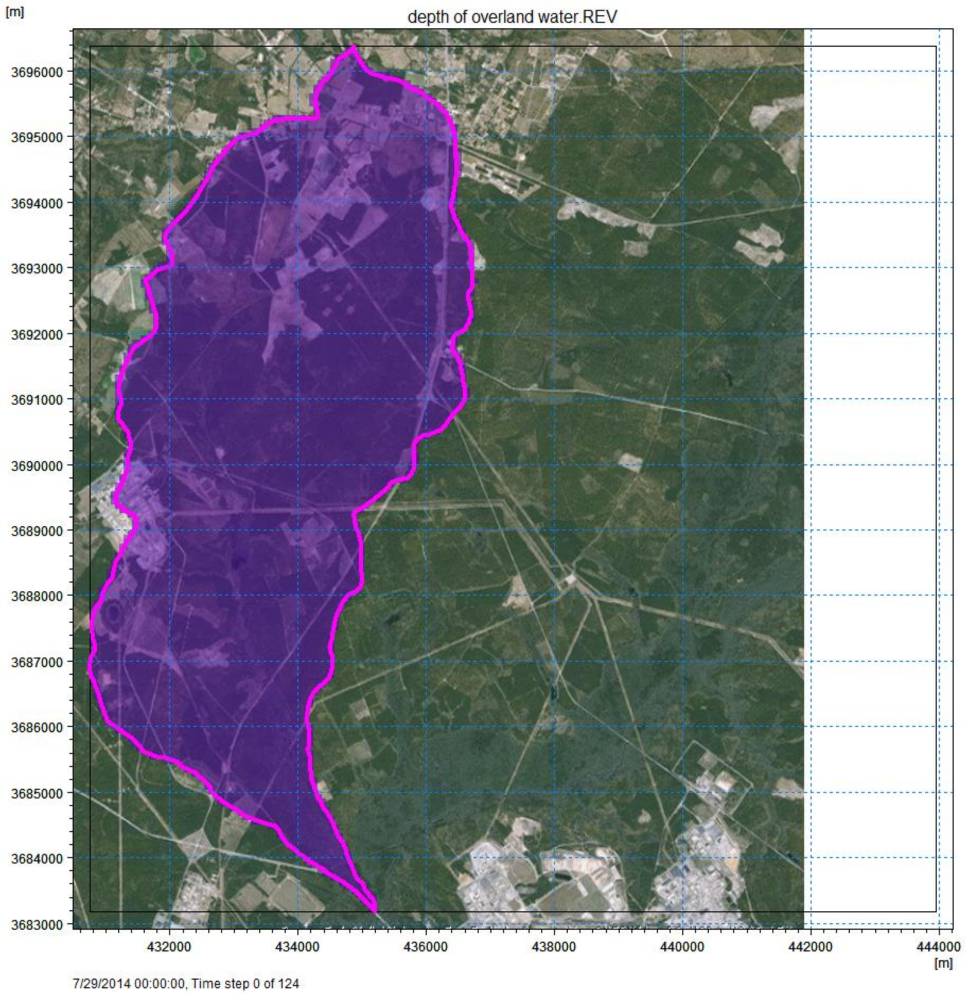
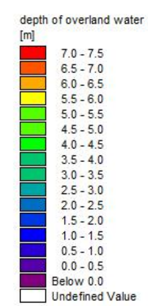
Subtask 3.1: Accomplishments



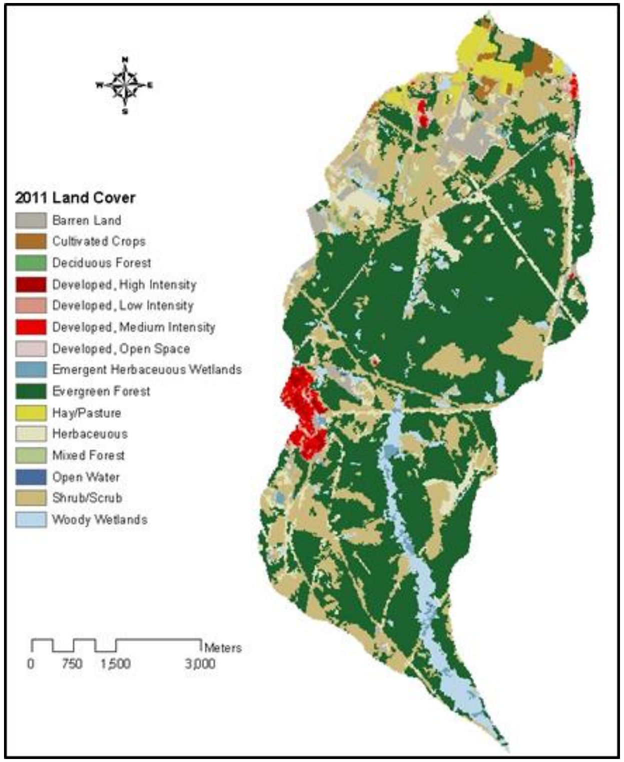


Simulation showing overland flow in a portion of the Tims Branch watershed

- Preliminary simulation results indicate that the model is capable of predicting flow depth and velocity within the study area during extreme climate events.

Subtask 3.1: Accomplishments

- **Land Use** module developed:
  - Includes both uniform and timeseries values of vegetation characteristics such as Leaf Area Index and Root Depth.
  - 15 vegetation classes identified.
  - Maps of Land Cover and Paved Runoff Coefficient developed.



Vegetation ID	LAI	RD (mm)
Barren Land	1.31	4000
Cultivated Crops	3.62	1500
Deciduous Forest	5.5	2000
Developed Low Intensity	2.5	2000
Developed Medium Intensity	2.0	2000
Developed Open Space	3.0	2000
Emergent Herbaceous Wetland	6.34	2000
Evergreen Forest	5.5	1800
Hay/pasture	1.71	1500
Mixed Forest	5.5	2400
Open Water	0.0	0.0
Quarries	1.31	4000
Transitional	1.31	4000
Urban/Recreational Grasses	2.0	2000
Woody Wetland	6.34	2000

Subtask 3.1: Accomplishments

- **Evapotranspiration (ET)** module developed:
  - Two methods employed: Richards Equation and Two-Layer Evapotranspiration/ Unsaturated Zone (ET/UZ).
    - a) Uniform values of reference ET, Leaf Area Index, and Root Depth
    - b) Station-based timeseries which requires timeseries of reference ET, and station-based rainfall.
  - Timeseries of rainfall acquired from SRS database.
  - Station-based timeseries of rainfall data from various stations within South Carolina used to generate rainfall grids in MIKE SHE. Data was pre-processed prior to input into MIKE SHE.
  - Station-based timeseries of reference ET acquired from stations within Aiken County near SRS. Data was pre-processed in accordance with MIKE SHE requirements.

ET Module Input Parameters

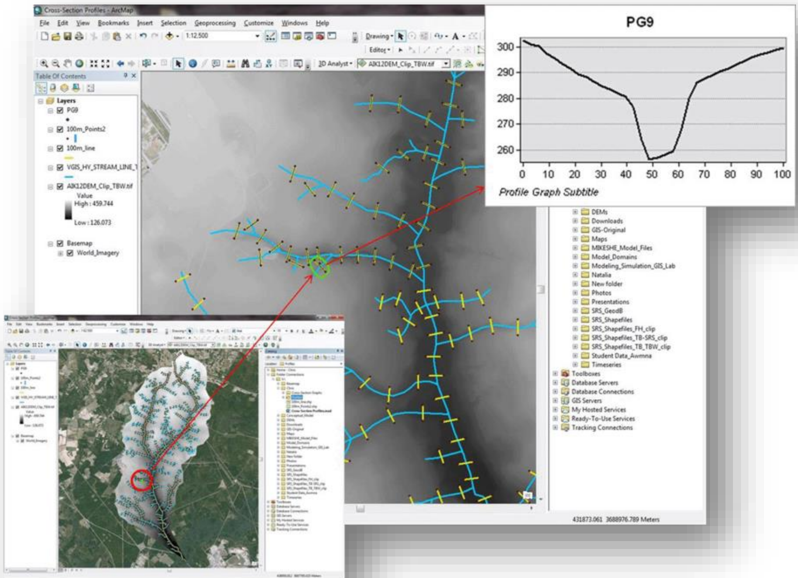
Values based on numerical stability criteria and experimental measurements reported in the literature.

Parameter	Value	Units
Detention Storage	2.5	mm
Surface-Subsurface Leakage Coefficient	0.0001	1/sec
Reference Evapotranspiration	2.22	mm/day
Leaf Area Index	1.3 – 6.3	m^2/ m^2
Root Depth	0.0 – 4000	mm

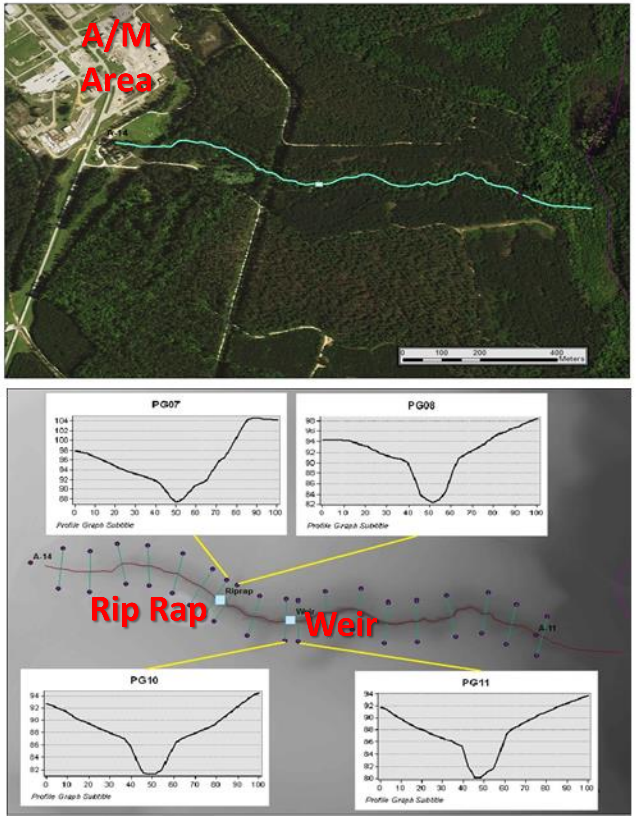
Subtask 3.1: Accomplishments

FIU Applied Research Center

- Began preliminary development of a 1-D stream/river hydrology model using MIKE 11.
- Network and cross-sections initially developed manually using GIS tools.



Cross sections of streams and tributaries in Tims Branch watershed (100 m) directly exported from ArcGIS into MIKE 11

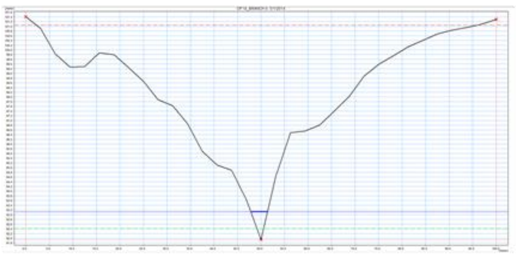


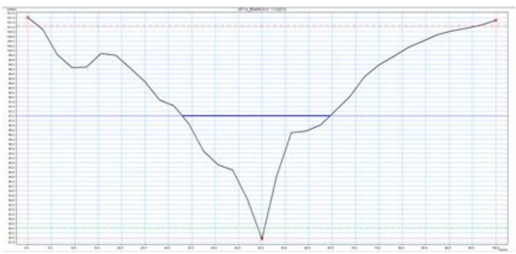
Cross sections (100 m) along A/M area outfall tributary near Outfall A-014 before and after control structures (rip rap & weir)

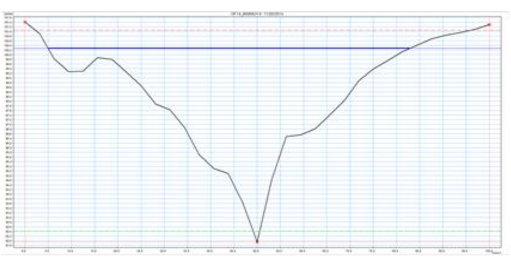
Subtask 3.1: Accomplishments

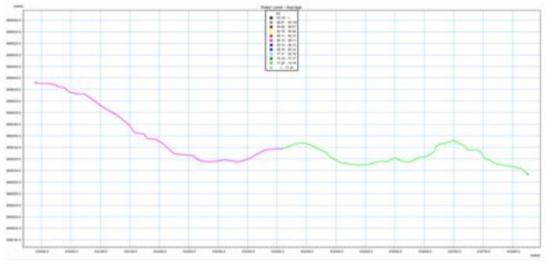
- MIKE HYDRO finally used to create the cross-sections automatically.

Water level animation at different times:



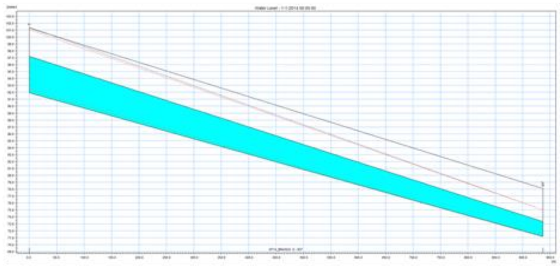






Average water level across Outfall 14 Branch

Water level timeseries at start and end points of branch



Water level profile at beginning of simulation

Volume Balance Summary

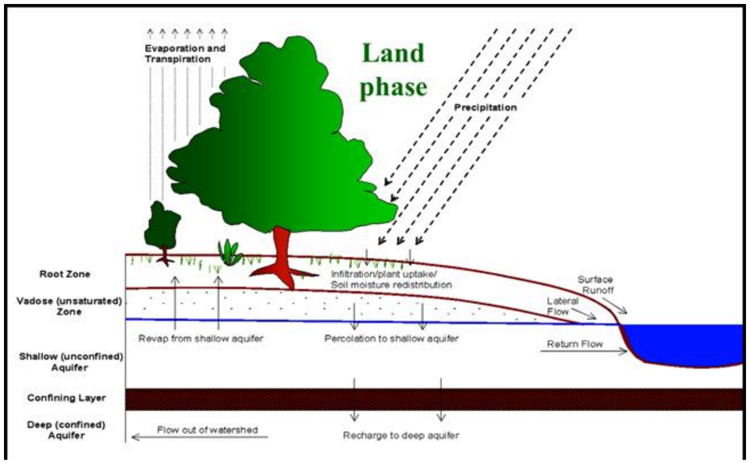
A: Initial volume in model area					**42910.16**	**m^3**
B: Final volume in model area					**87650.62**	**m^3**
Lateral sources inflow	0.00	m^3				
Lateral correction	0.00	m^3				
Open boundaries inflow	19879803833.39	m^3				
C: Total inflow					**19879803833.39**	**m^3**
Lateral sinks outflow			0.00	m^3		
Open boundaries outflow			19879780217.73	m^3		
D: Total outflow					**19879780217.73**	**m^3**
E: Continuity balance = B-A-C+D =					**21124.81**	**m^3**
Relative deficit E/max(A,B,C,D) =					**0.00**	0

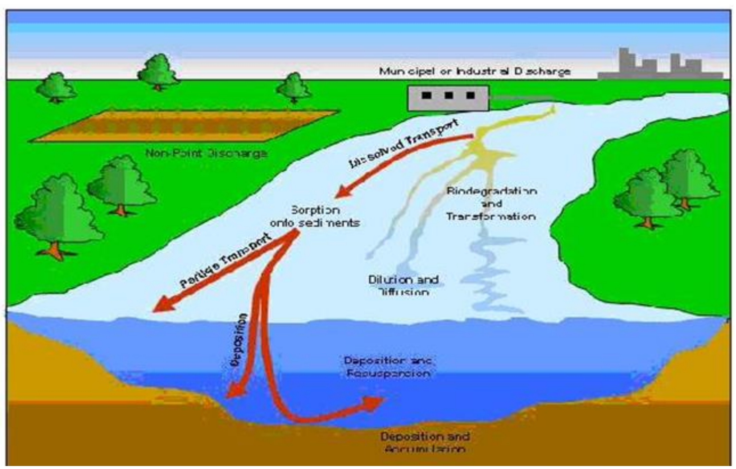
Water volume balance summary

Preliminary MIKE 11 simulation results

Subtask 3.1: Accomplishments

Hydrology Modeling using SWAT





- A comparative model is being developed using the Soil and Water Assessment Tool (SWAT).
- SWAT is a river basin scale model developed to predict the impact of land management practices on water, sediment and agricultural chemical yields.
- SWAT is a public domain model actively supported by the USDA at the Grassland, Soil and Water Research Laboratory in Temple, Texas.
- SWAT is physically based, computationally efficient and capable of simulating very large basins.
- SWAT can be used to study long-term impacts.

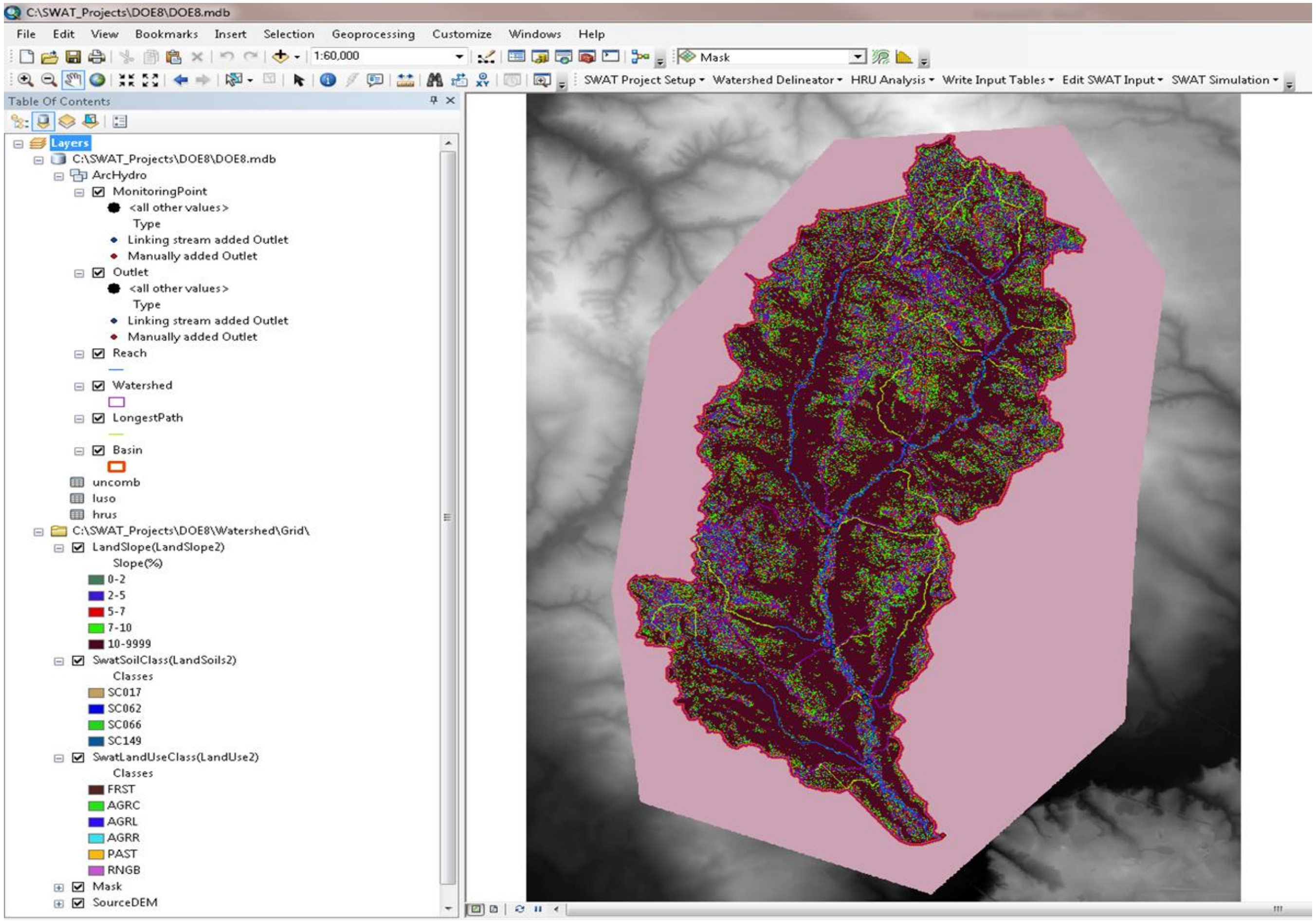
Subtask 3.1: Accomplishments

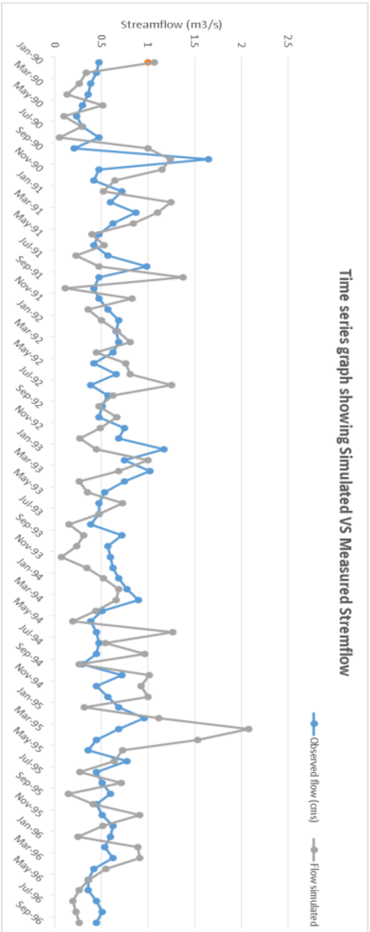
FIU Applied Research Center

- Similar to MIKE SHE/11, the SWAT model also has a user interface that accepts GIS input files including:
  - Digital elevation model (DEM)
    - To delineate basin and sub-basin boundaries
    - To calculate sub-basin average slopes and delineate the stream network
  - Land cover and soil shapefiles
    - For input of land use, soil and slope parameters
    - To create and define Hydrological response units (HRU's).

Subtask 3.1: Accomplishments

Implementation of SWAT model for Tims Branch watershed





Subtask 3.2: Application of GIS technologies for hydrological modeling support

Angelique Lawrence
Natalia Duque (DOE Fellow)
Awmna Rana (DOE Fellow)

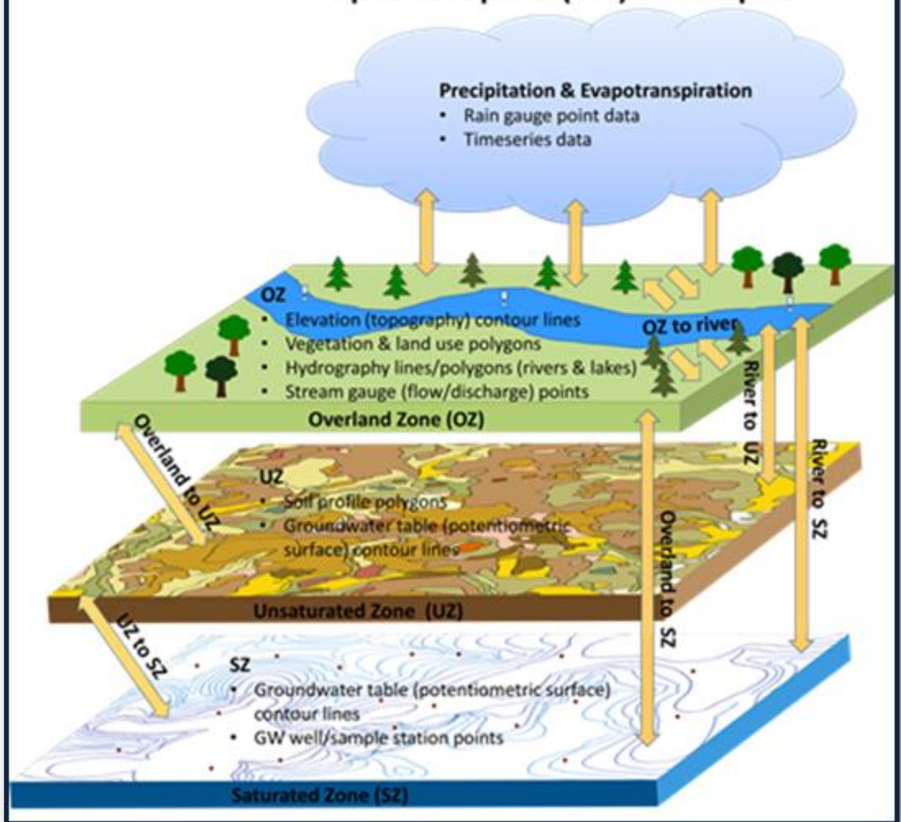
Florida International University

Subtask 3.2: Accomplishments

FIU Applied Research Center

- Hydrological model development is heavily supported by the use of GIS technology.
  - Geodatabases for storage and management of data.
  - ArcGIS geoprocessing tools for preparation of spatiotemporal model data.
  - Geospatial analysis of environmental data.
  - Maps and graphs for visualization of input data and model results.

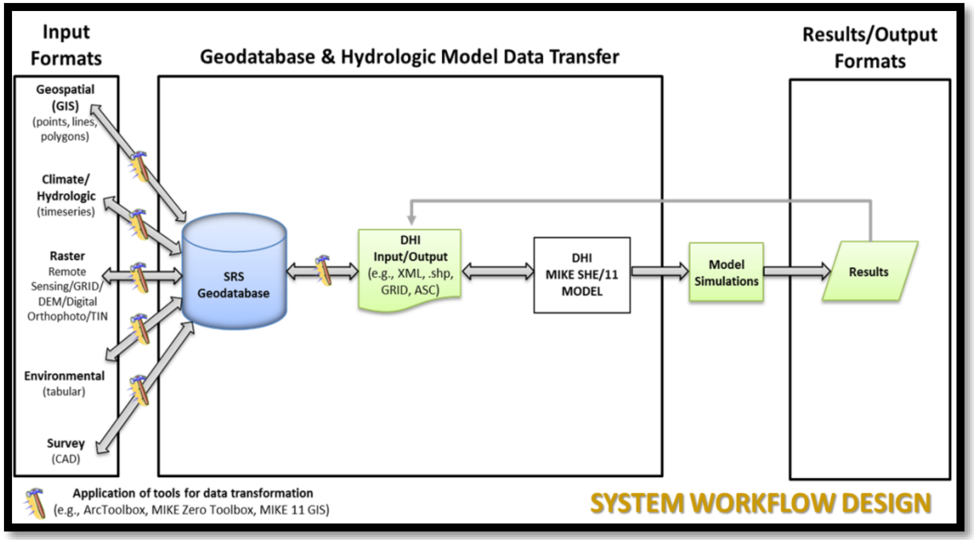
Fig. 3. MIKE SHE Model Spatiotemporal (GIS) Data Inputs



Subtask 3.2: Accomplishments

FIU Applied Research Center

- A geodatabase was developed to store and manage the data used for hydrological model development.
- ArcGIS Diagrammer was used to document the contents of the geodatabase in a simple report format.



ArcGIS Diagrammer

Report Creation

Date	Thursday, April 10, 2014
Author	Lawrence/ARC-2481F4A8 on ARC-2481F4A8

System Information

Operating System	Microsoft Windows NT 6.1.7601 Service Pack 1
.Net Framework	2.0.50727.5477
Diagrammer	10.0.1.0

Geodatabase

Workspace Type	Database Connection
File	C:\Users\lawrence\AppData\Roaming\ESRI\Desktop10.2\ArcCatalog\ORR_GeodB.sde

Data Report

ObjectClass Name	Type	Geometry	Subtype	Total	Extent	Snapshot
ORR_GeodB.DBO.Admin_Features						
ORR_GeodB.DBO.domain_EFPC	Feature Class	Polygon	-	1	745462.4274 759759.336000003 177890.026900001 189776.924400002	
ORR_GeodB.DBO.domain_WOC	Feature Class	Polygon	-	1	749813.855999999 754110.923500001 176776.130800001 181566.498199999	
ORR_GeodB.DBO.ORR_Boundary_Polygon	Feature Class	Polygon	-	1	740897.648000002 762737.393299997 172436.423 186361.8125	
ORR_GeodB.DBO.Scrap_Yard	Feature Class	Polygon	-	2	755860.313600004 756112.826300003 183999.275899999 184279.2322	
ORR_GeodB.DBO.Scrapyard	Feature Class	Polygon	-	2	755784.380199999 756009.423900001 184038.085099999 184256.5099	
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ORR_GeodB.DBO.UBC	Feature Class	Polygon	-	1	754811.278700002 756109.7293 182843.792300001 184434.851500001	
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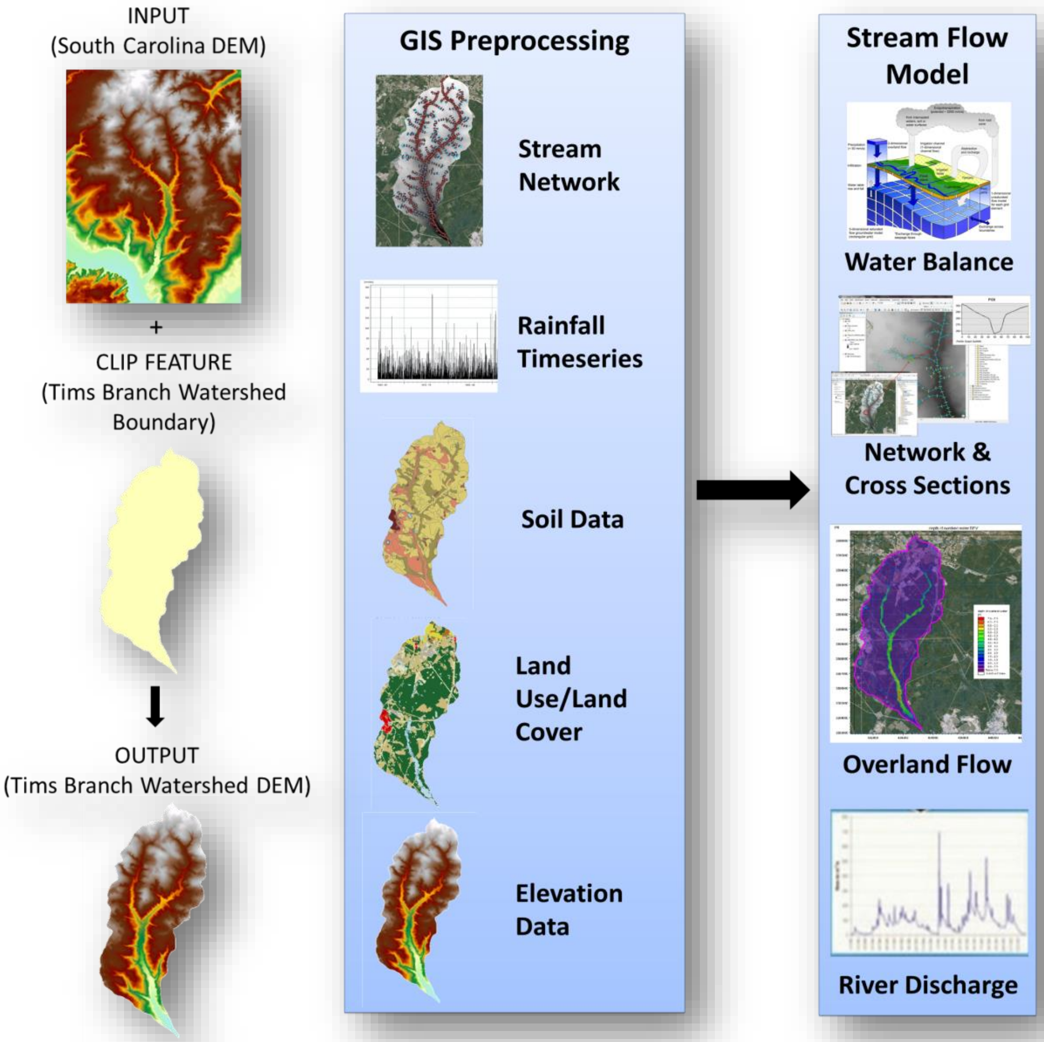
ORR_GeodB.DBO.UEFPC	Feature Class	Polygon	-	1	755561.088200003 759767.336599998 183520.449700002 186574.551800001	

Subtask 3.2: Accomplishments



- Utilized ArcGIS tools to preprocess data derived from SRS/SRNL and other federal agency online databases such as USGS, & USDA (NRCS/NLCD).
- Downloaded data projected to relevant coordinate system and clipped to model domain.
- ArcGIS ModelBuilder used to automate repetitive tasks and document geoprocessing workflow. Process flow models developed are reusable tools that can be implemented for other DOE sites.

Subtask 3.3: Biota, biofilm, water and sediment sampling in Tims Branch

Florida International University

Subtask 3.3: Accomplishments

- This task includes additional sample collection of biota, biofilm, water and sediment in Tims Branch for analysis of total mercury and tin in tissue, biofilm and sediment; and possible speciation analysis on sediment for mercury, tin and other elements (e.g., uranium).
- This will serve to monitor and document any impacts of the innovative stannous chloride air stripping technology and provide additional data to assist with hydrological model calibration and validation.
- The sampling will be initiated by FIU students during their summer 2016 internship at SRNL/SREL and continued if necessary throughout the year by FIU students and/or ARC researchers.
- Collaboration has already been initiated with SRNL and SREL to support this effort.

Task 3: Future Work (FIU Performance Year 6)

- Complete input of MIKE SHE model configuration parameters for simulation of unsaturated flow.
- Complete input of MIKE SHE model configuration parameters for simulation of flow in the saturated zone.
- Sample and data collection and analysis from Tims Branch.
- Progress Report for Subtask 3.1: Modeling of surface water and sediment transport in the Tims Branch ecosystem.
- Progress Report for Subtask 3.2: Application of GIS technologies for hydrological modeling support.

Task 4:
Sustainability Plan for the A/M Area Groundwater Remediation System

Dr. David Roelant
Natalia Duque (DOE Fellow)
Yoel Rotterman (DOE Fellow)

Florida International University

Task 4: Description

This task supports US DOE EM-13 in developing plans for improving active remediation systems to improve performance while lowering resources (money, GHSs, energy) used. The initial effort identified specific improvements to the SRS A/M Area groundwater remediation system with expectation that it would apply to many “pump and treat” systems across DOE. Under “Sustainable Remediation” sustainability metrics are identified and included into environmental management decisions.

Benefits:

- Provides state of the practice tools (developed for DOD sites) for analysis of sustainable and green remediation alternatives, which are needed to address long-term sustainability in terms of reduced environmental and energy footprints of remedial actions and operating systems.
- Greatly lowers costs and improves effectiveness of remediation strategies applicable to soil, groundwater, radioactive waste, and facility D&D.
- Helps identify alternatives for remediation, monitoring, waste handling, and D&D design that save money and support sustainable, compliant decision-making.
- Identifies sustainability factors for the investigation, construction, operation, and long-term monitoring phases to estimate footprint of alternatives.
- Provides a decision matrix for remedy selection, design, or implementation and allows for remedy optimization.

Fig. 1: M-1 Air Stripper System at SRS A/M Area

Task 4: Results 2014

Collection of per Well Data

- Major effort in 2014 was identification of missing data per well on TCE & PCE recovery.
- Site had detailed info on water going to stripper from all wells combined.
- Site had a detailed database with 90% of the per well data.
- Site supplied dozens of reports from which FIU located most of the missing per well data to allow for per well analyses.

Results per Well

- Monthly removal rate and cumulative mass removed for TCE and PCE in the 12 recovery wells were analyzed for 1987-2012.
- 7 of 12 recovery wells have transitioned to more PCE than TCE removed. This is an expected result since TCE was initially used and then replaced by PCE.
- Rate of recovery in some wells affected by Dynamic Underground Stripping (DUS) process.
- 7 wells exhibit exponential decay in contaminant removal, 5 exhibit steady concentrations, and 2 exhibit linear decreases.

Task 4: Results 2014

DUS still affecting remediation today

- Dynamic Underground Stripping (DUS) process injected steam into the ground and enhanced recovery of VOCs that is ongoing today.
- Steam injection occurred August 2005 – 2009.
- Steam was applied to the deep vadose zone first, then to the aquifer zone, and then to the mid-vadose zone.
- Soil vapor extraction is ongoing, residual temperatures in the deep low permeability zones still exceeding 65.6°C (150°F).
- To date >204 metric tons (450,000 lb) of VOCs removed.

FIU Applied Research Center

Task 4: Predicted recovery of TCE & PCE over time

Source: SRNL

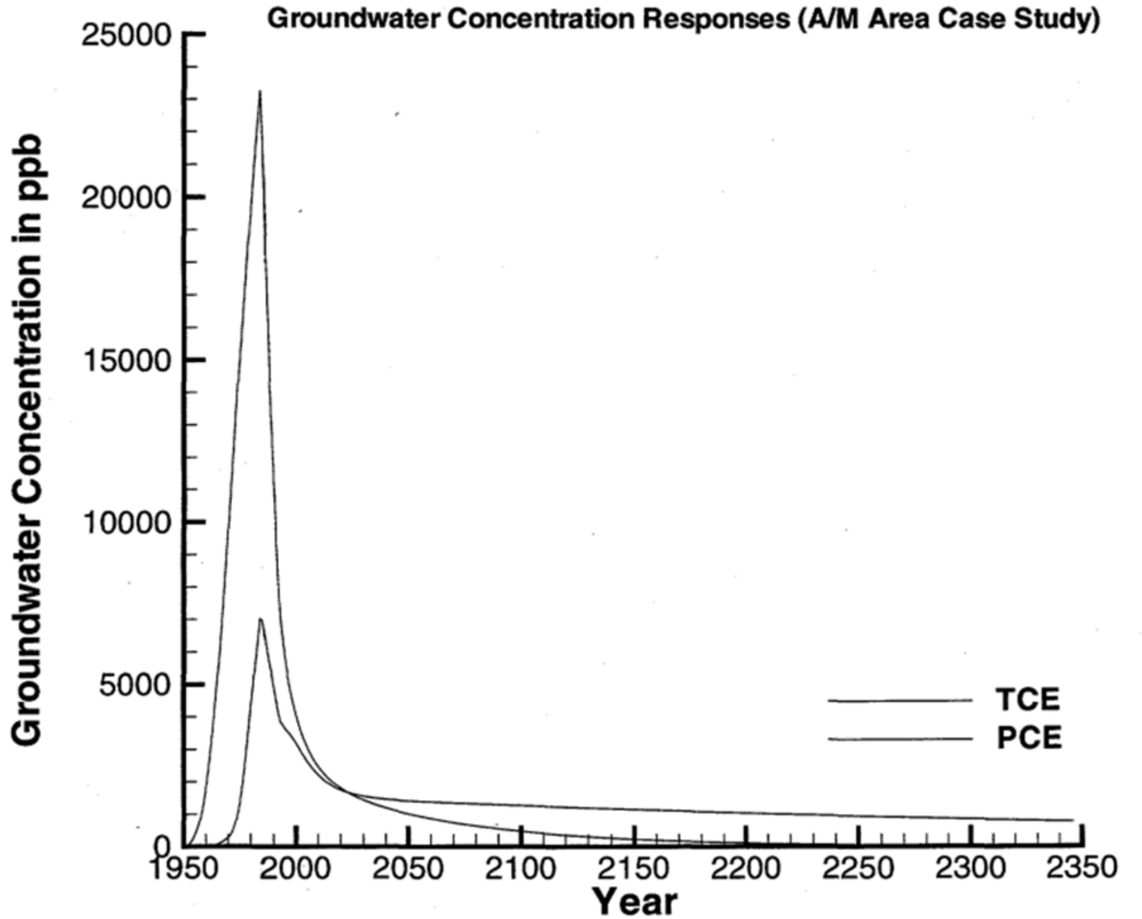
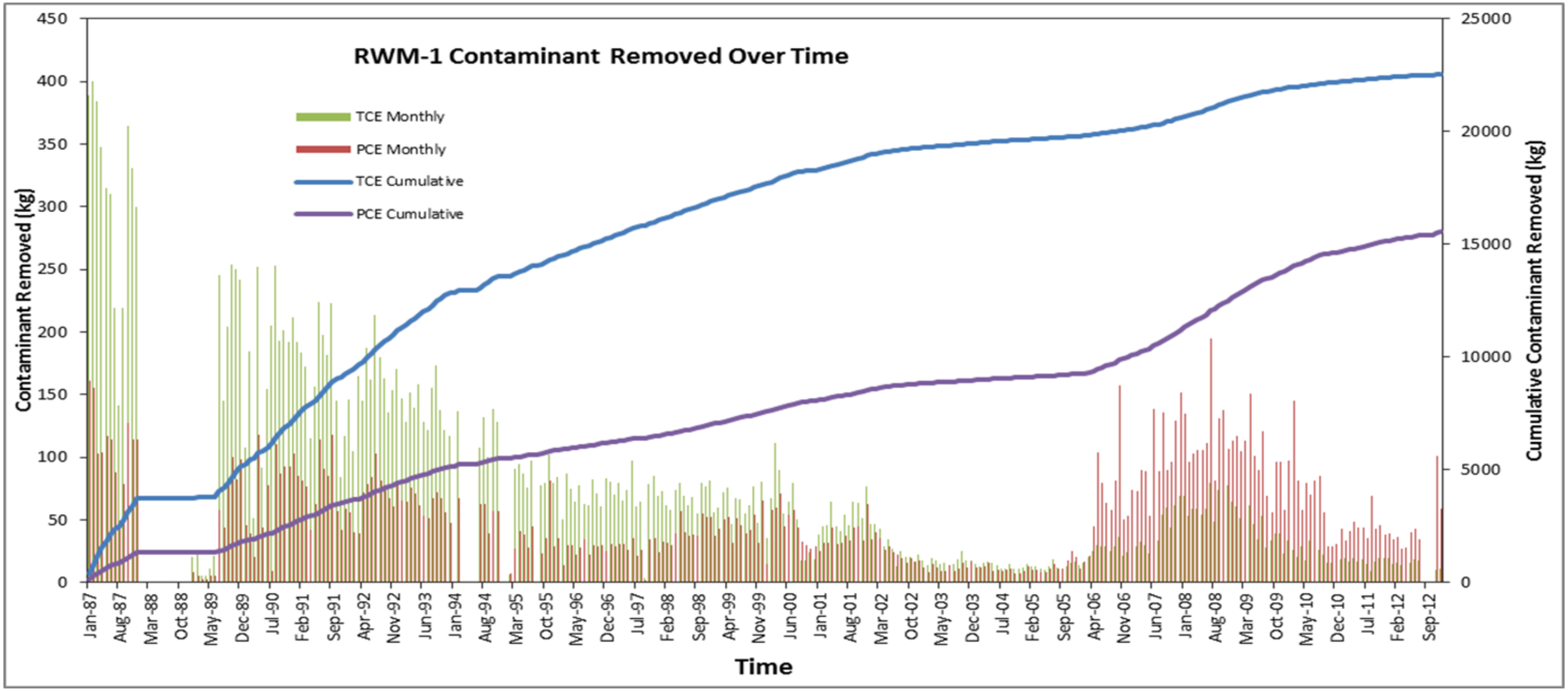


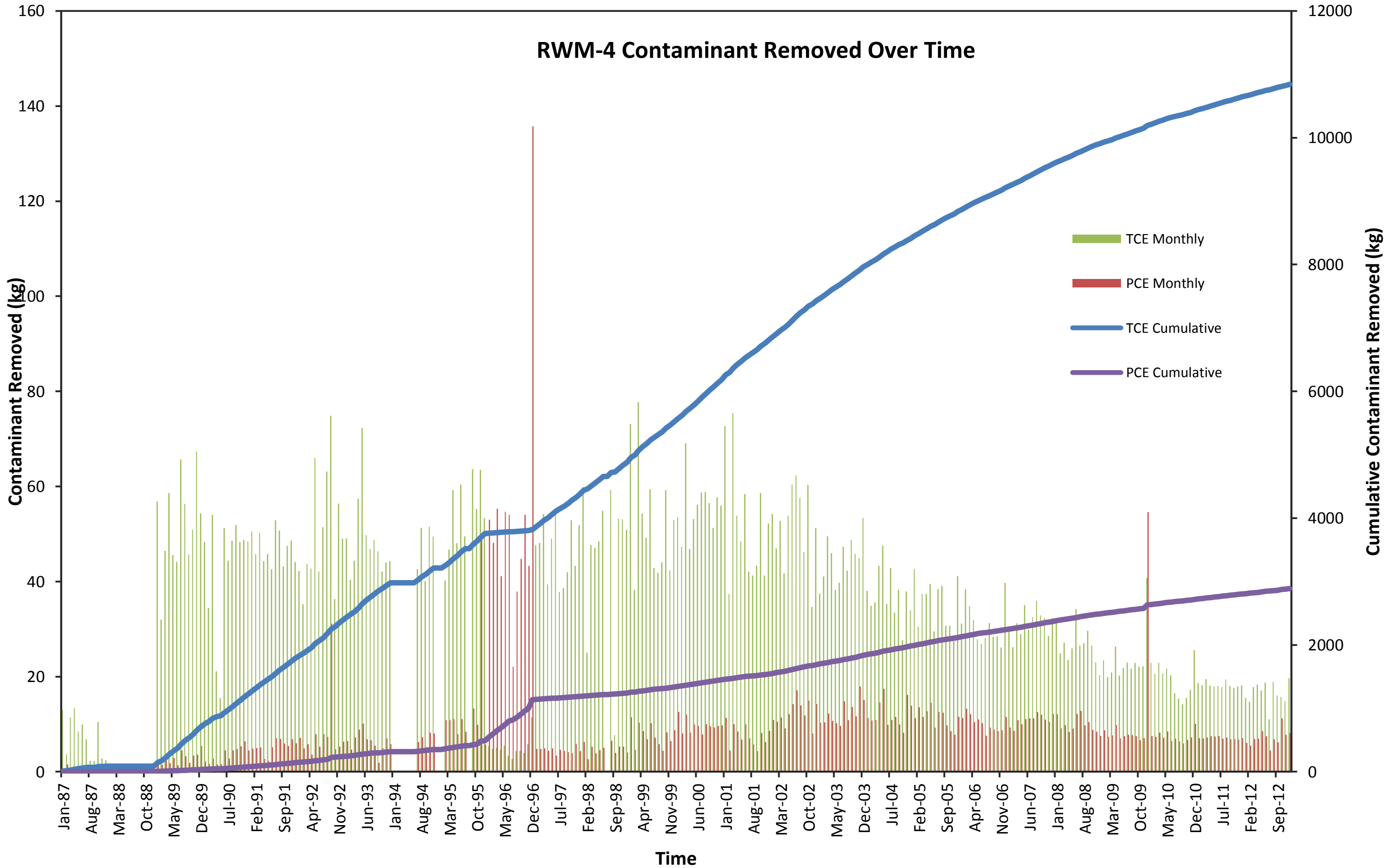
Figure 50: Response of Bulk Groundwater Concentrations to the A/M Area Corrective Action Program.

Task 4: Results 2014

FIU Applied Research Center

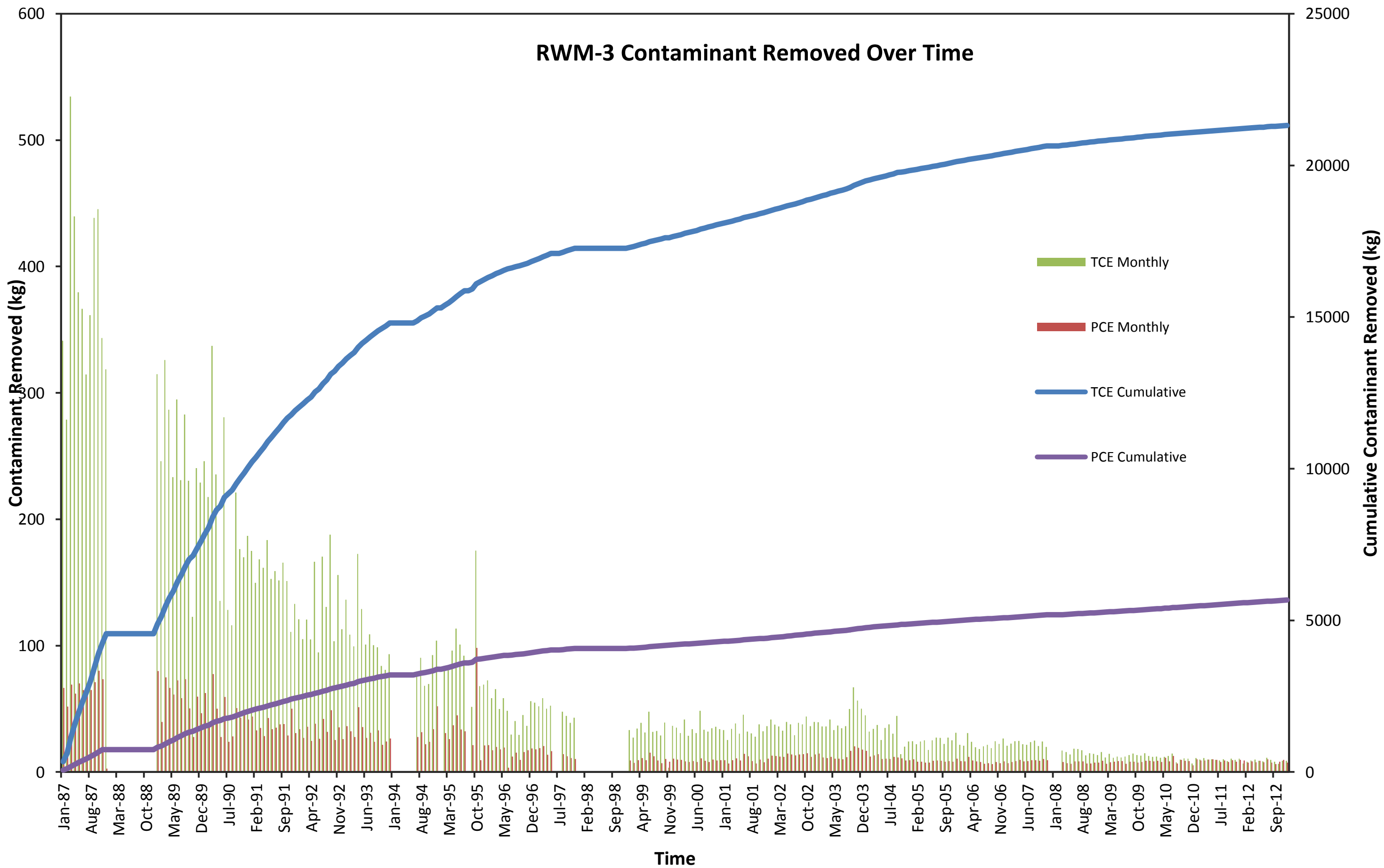


Task 4: Results 2014



Task 4: Results 2014

FIU Applied Research Center



Task 4: Accomplishments

FIU Applied Research Center

- Completed five Sustainable Remediation Papers:
  - *Green and Sustainable Remediation Practices, Tools and their Application at DOE Office of Environmental Management Sites.*
  - *Baseline Summary Report for Sustainable Remediation Options for M1 Air Stripper at DOE SRS.*
  - *Sustainability Analysis for the M1 Air Stripper and Pumps of the M Area Groundwater Remediation System at DOE SRS*
  - *Green and Sustainable Remediation Options for the M Area Groundwater Remediation System at SRS.*
  - *A Preliminary Green and Sustainable Remediation Analysis of the M1 Air Stripper at DOE's Savannah River Site, Waste Management, Mar. 2016.*
- Sustainability analyses resulted in these 4 primary recommendations:
  - Utilization of a solar photovoltaic system for powering the A/M Area groundwater remediation system.
  - Further analysis to determine an optimal speed for the blower motor that is sufficient to run the countercurrent stripper and removes the volatile organic contaminants to below the 1 ppb required.
  - Groundwater modeling analysis to optimize the pumping rate for each recovery well and for the entire system that provides hydrologic containment and maximizes the concentration of contaminants pumped to the stripper with lower total groundwater and air flow rates.
  - Replacement of groundwater pumps when they fail with lower power pumps that match the required pump rate of the recovery well (e.g., additional lower powered 1-5 HP pumps).

Task 4: Future Work

- Final report was delivered to DOE EM and SRNL on Dec. 15, 2015 completing this task.
- No additional effort is planned on this task

Task 5: Remediation Research and Technical Support for WIPP

Hilary P Emerson (FIU-ARC)
Timothy Dittrich (LANL)
Michael Richmann (LANL)

Don Reed (LANL Team Leader) Russ Patterson (DOE-CBFO)

Research performed at the Carlsbad Environmental Monitoring and Research Center (CEMRC) operated by New Mexico State University

Florida International University

FIU Applied Research Center

Task 5: Collaboration Goals

Objective: To further our understanding of the sorption of trivalent actinides and lanthanides in WIPP-relevant minerals

Initiate Collaboration

- LANL postdoc (Tim Dittrich) and ARC postdoc (Hilary Emerson)
- Fall 2015

Deploy FIU-ARC postdoc

- 8 weeks as a visiting scientist
- Learn to conduct mini columns
- Feb – Apr 2016

Conduct parallel experiments

- Parallel experiments with more basic science focus at FIU
- 2016-2017

Long-term partnership

- Continue WIPP-related research as part of the DOE-EM cooperative agreement
- 2017 and beyond!

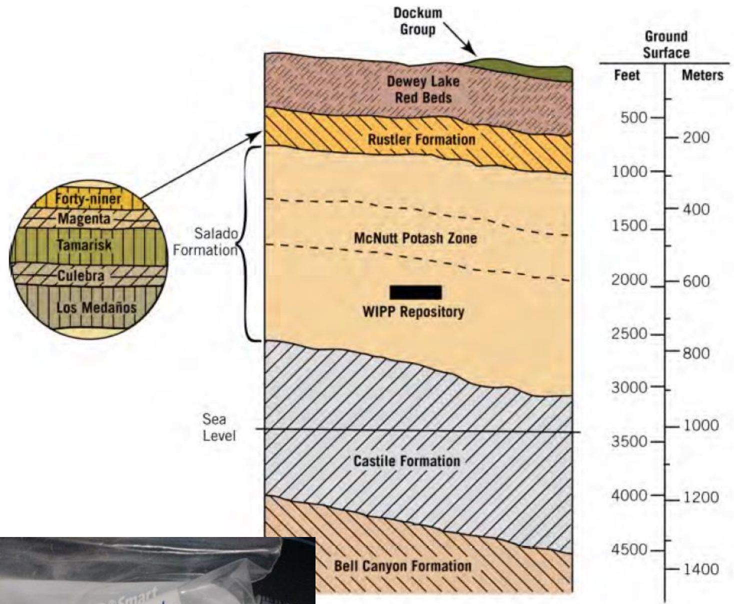
Task 5: WIPP Release Scenario

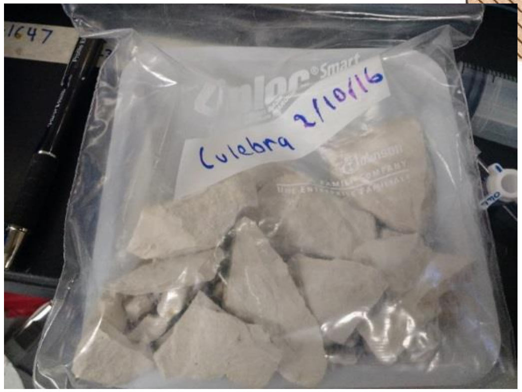
- Human Intrusion is most likely per cuttings, cavings or spallings

  * leads to direct and/or long-term brine release

- Horizontal brine release through Rustler formation (most transmissive)

  * Most permeable layer- Culebra dolomite [$CaMg(CO_3)_2$]





Task 5

Objective: To update experimental sorption data for Trivalent An/Ln

- Oxidation states – III > IV >> VI >> V
- Release – Pu ~ Am >> U > Th >> Np ~ Cm

Oxidation State Distribution of Key Actinides in WIPP Performance Assessment

Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Plutonium	50%	50%			Am/Nd for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium

Task 5

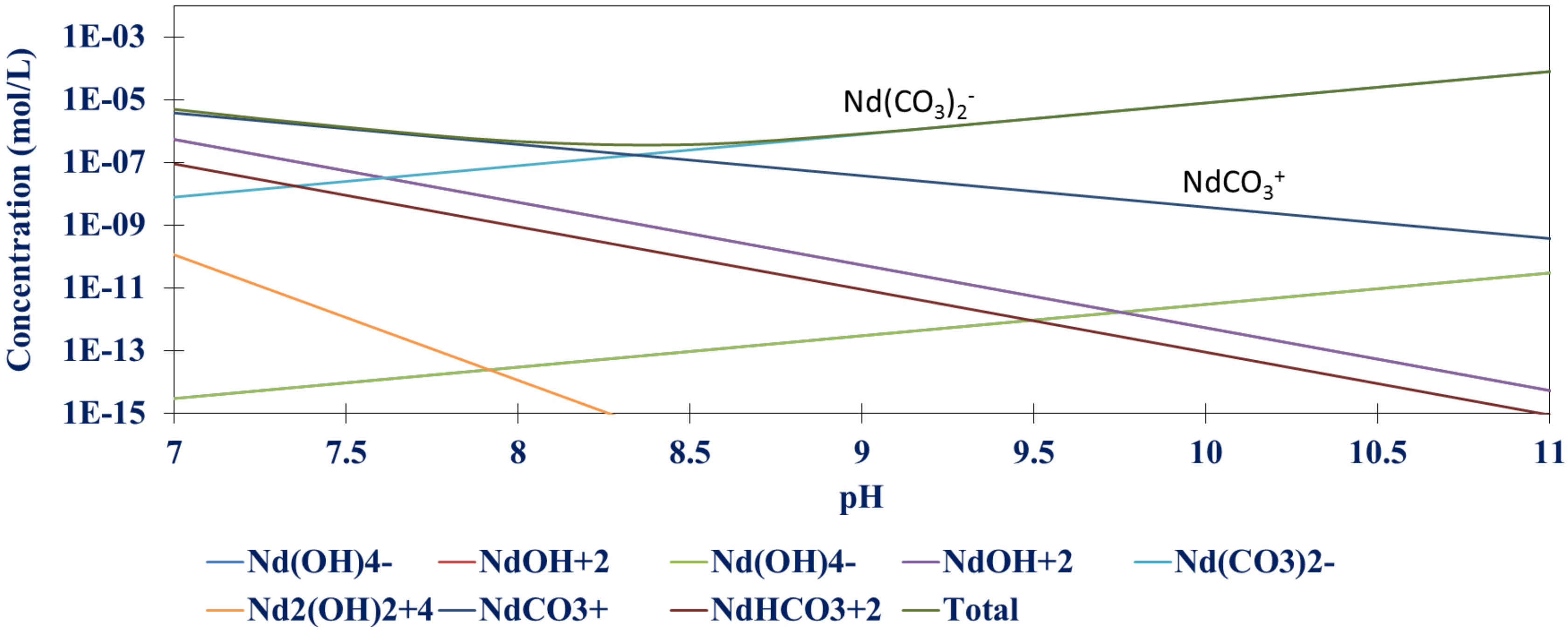
Lack of Experimental Sorption Data for Trivalent An/Ln for Dolomite

- Previous work: LogK_d's for dolomite reported from 3.4 – 6
  - **Brady *et al*. 1999**: limited residence time reactor measured K_d's, *exceeded Nd solubility* for pH 6 – 8, *limited pH range* for Am(III) (pH 3 – 6), *limited conditions* (0.05 and 0.5 M NaCl)
  - **Perkins *et al.* 1999**: intact-core experiments, *no breakthrough* recorded after many months of injection, *possible precipitation* of Am(III)
  - **Brush and Storz 1996**: batch sorption experiments in brines, *no pH reported* for Am(III) K_d's, *limited* Nd(III) K_d's for atmospheric CO_2 in 0.05 M NaCl

Task 5

Neodymium Speciation

in the Presence of Atmospheric CO_2



Note: solubility is low (~50 ppb with atmospheric CO_2 and ~20 ppb without)

Two major species: $NdCO_3^+$ and $Nd(CO_3)_2^-$

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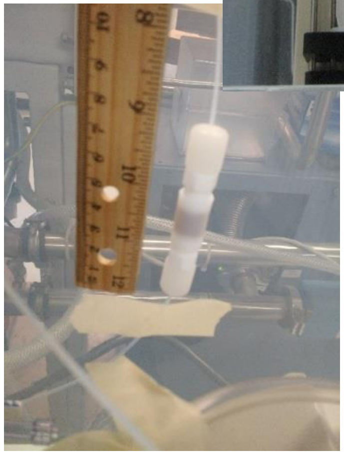
Task 5
Materials and Methods

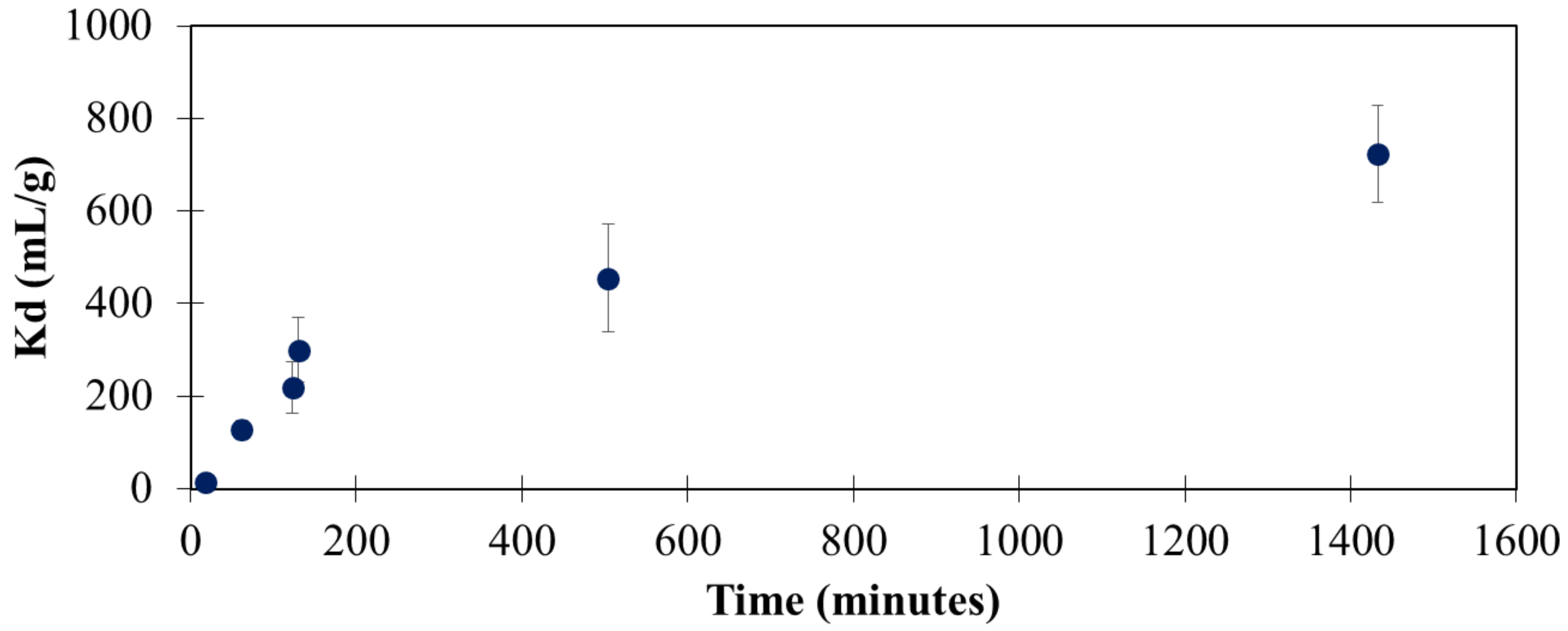
- Focus is *simplified* brines, i.e. NaCl
- **Batch sorption** (Equilibrium and kinetics)
  - Initially 20 ppb Nd
  - 5, 25 and 100 g/L dolomite
  - 0.01 - 1.0 M IS (3 mM $NaHCO_3$ + NaCl)
  - Target pH 8.6
- **Continuous injection mini columns**
  - 1 cm column (~1 gram dolomite, porosity 0.32)
  - 0.01, 0.1 and 1.0 M IS (3 mM $NaHCO_3$ + NaCl)
  - 20 ppb Nd
  - Target pH 8.6



Task 5

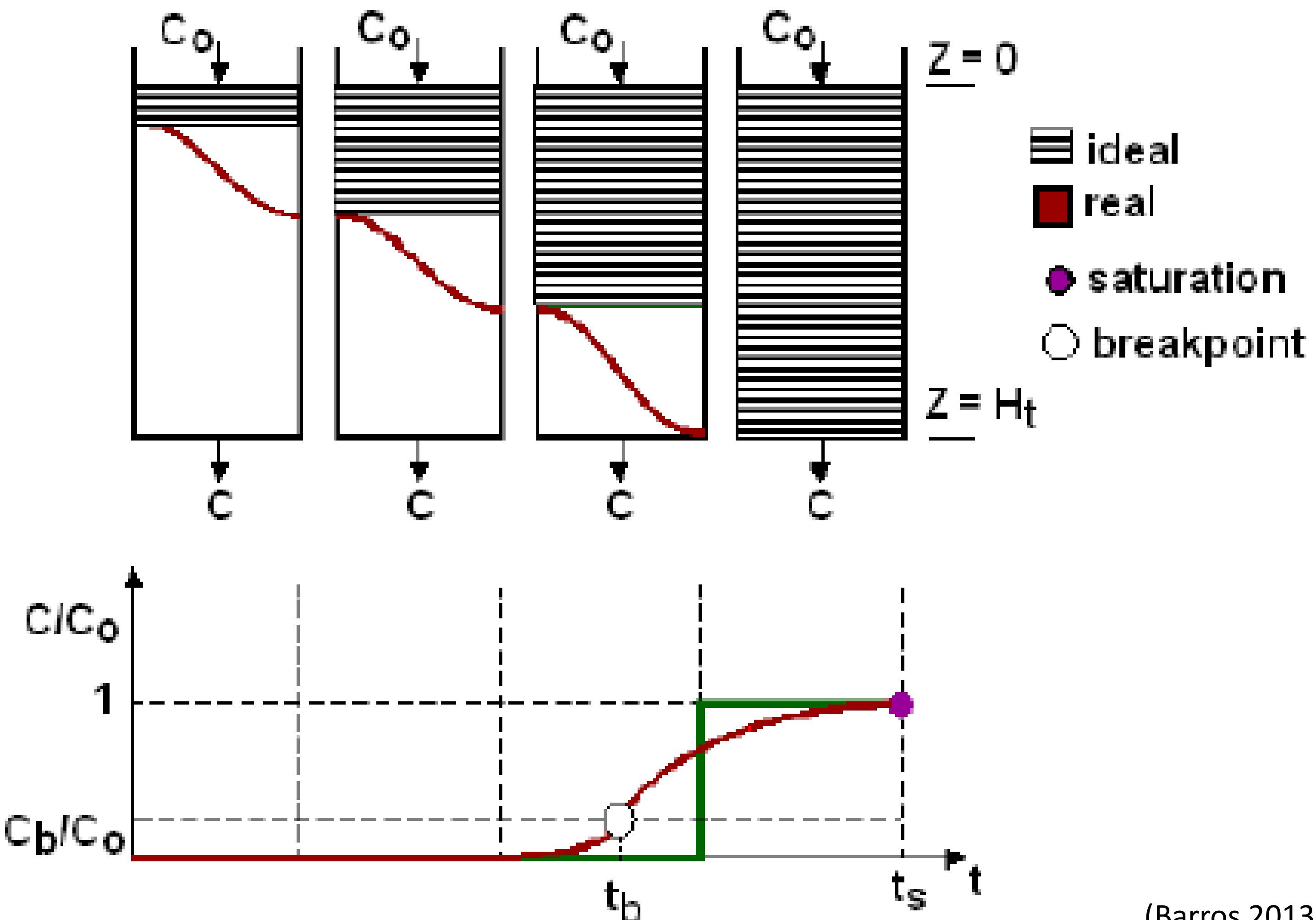
Preliminary Batch Experiments

20 ppb Nd(III) – 0.097 M NaCl + 0.003 M $NaHCO_3$



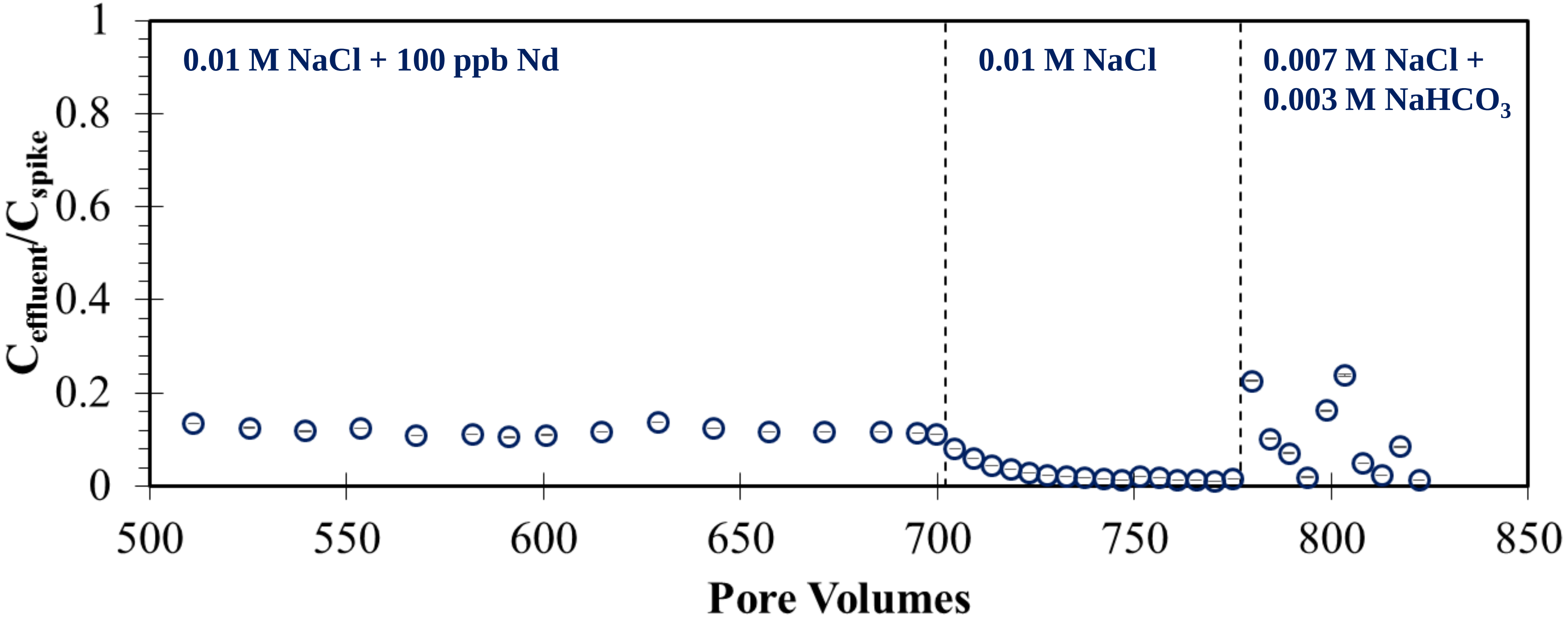
Note: Appears to follow first order kinetics up to 200 minutes, then kinetics slow

Task 5
Column Breakthrough
Expected Results



(Barros 2013)

Task 5
Preliminary Column Breakthrough
0.01 M NaCl – 100 ppb Nd(III)

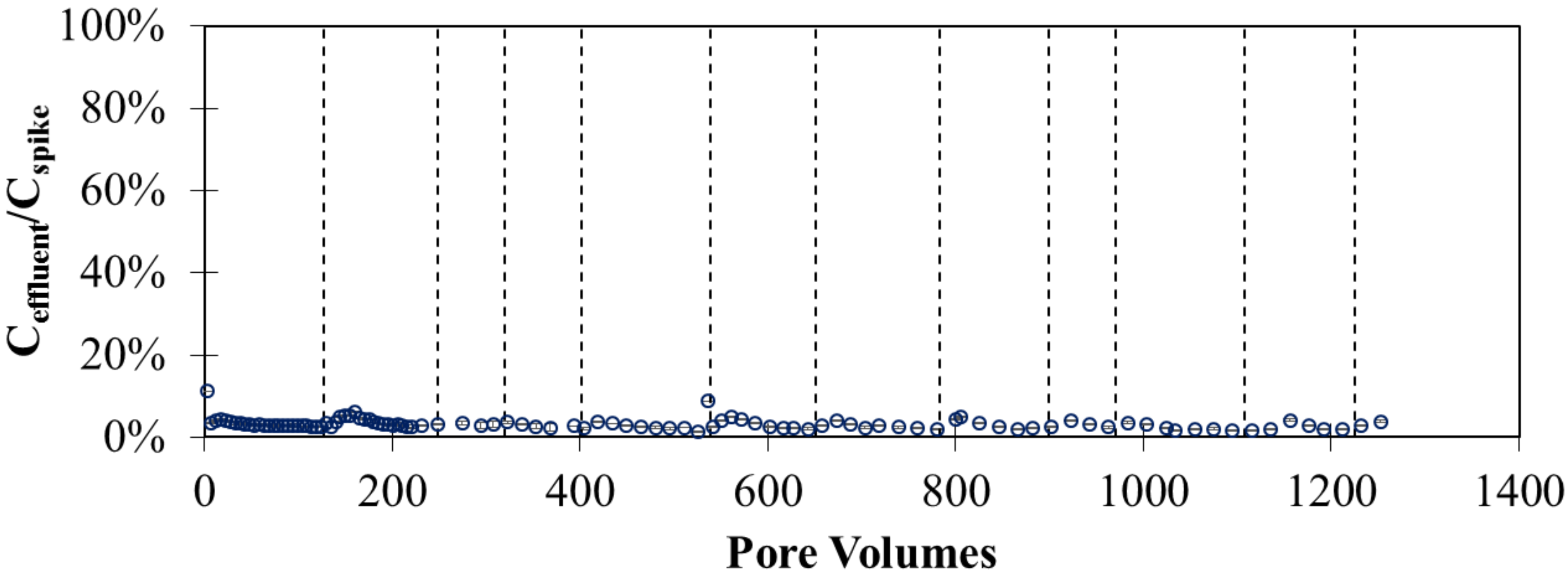


Column retention time ~18 minutes

Task 5

Preliminary Column Breakthrough

0.097 M NaCl + 0.003 M $NaHCO_3$ – 20 ppb Nd(III)



$$R = 1 + \frac{\rho_B}{\theta} K_d$$

Pore volumes > 1280 → K_d > 140 mL/g

Task 5

Preliminary Conclusions and Future Work

- **Preliminary Results**
  - Sorption is very strong in batch systems (consistent with previous work), Kd's > 10^3
  - >700 pore volumes of Nd continuously injected at 20 ppb without reaching saturation of mini columns (1 cm length, 1 gram dolomite)
- **Future Work**
  - Write an internship report
  - Experiments will be continued in parallel with LANL
  - Continue 0.01M – 1M [NaCl + 3 mM $NaHCO_3$] column and batch experiments with 20 ppb Nd [1.2×10^{-7} M]
  - Model results via PHREEQC
  - Am(III) for comparison to our trivalent analog, Nd(III)
  - Relevant ligands? EDTA, DFOB, oxalic acid?

Task 5

FIU – LANL Collaboration

Status Update

Accomplishments

- Learned mini column experimental protocols
- Conducted batch sorption and column saturation experiments in the presence of 20 ppb Nd(III) at 0.01, 0.1 and 1.0 M ionic strength (3 mM $NaHCO_3$ + NaCl) at pH ~8.6

Next Step

- Parallel experiments to be conducted at LANL Carlsbad and FIU-ARC
- Further exploration of trivalent actinide and lanthanide (Nd, Am, Pu) sorption to WIPP relevant minerals in the presence of ligands, variable redox conditions

Project 2 Future Work (FIU Performance Year 7)

- Task 1:
  - Complete dissolution and sequential extraction experiments.
  - Biodissolution of sodium autunite; effect of bacteria consortia on the dissolution.
  - Effect of variable uranium and bicarbonate concentrations on the U(VI) partitioning on Hanford soil minerals; soprtion kinetics.
  - Column experiments on the influence of microbial activity on the corresponding electrical geophysical response after ammonia injections in the vadose zone.
- Task 2:
  - Elucidate U(VI) – soil interactions and the effect of different soil fractions.
  - Kinetic experiments for sorption of U(VI) with and without HumaK.
  - Synergetic interactions of humic acid and colloidal silica on uranium removal under varying pH and uranium concentrations.
  - Study the migration and distribution of other commercially available HA and obtain sorption and desorption parameters under different pH levels; Develop coupling between flow and transport of the contaminant in the subsurface.
- Task 3:
  - Model calibration and validation.
  - Couple MIKE SHE and MIKE 11.
- Task 4:
  - This task has been completed. Sustainable remediation support will be provided to the DOE EM student challenge under Project 4.
- Task 5:
  - Continue WIPP-related research as part of the DOE-EM cooperative agreement.

Project 2: Masters & PhDs

- Claudia Cardona: PhD Environmental Engineering
  - Expected graduation date: Summer 2016
- Natalia Duque: MS Water Resources Engineering
  - Expected graduation date: Fall 2016
- Silvina Di Pietro: PhD Chemistry
  - Expected graduation date: Fall 2019
- Hansell Gonzalez: PhD Chemistry
  - Expected graduation date: Fall 2017
- Sandra Herrera: MS Environmental Engineering
  - Expected graduation date: Spring 2016
- Robert Lapierre: MS Chemistry
  - Expected graduation date: Summer 2016

Project 2: Internships (Summer 2015)

- Claudia Cordona
  - Location: PNNL, Richland, WA
  - Summer Site Mentor: Dr. Jim Szecsody, PNNL
  - “Geochemistry Related to NH_3 Gas Used for Uranium Remediation in the Vadose Zone”
- Natalia Duque
  - Location: SRNL, Aiken, SC
  - Summer Site Mentor: Dr. Ralph Nichols, SRNL
  - “Analysis of Solar Generated Power in the Southeastern United States”
- Kiara Pazan
  - Location: SRNL, Aiken, SC
  - Summer Site Mentors: Dr. Miles Denham & Margaret Millings, SRNL
  - “Processing of Diffusion Samplers to Test Remediation of Uranium by Humate”
- Aref Shehadeh
  - Location: SRNL, Aiken, SC
  - Summer Site Mentor: Dr. Miles Denham, SRNL
  - “Optimizing Remediation of I-129 using AgCl Colloidal-Sized Particles in SRS F-Area Sediments”
- Yoel Rotterman
  - Location: SRNL, Aiken, SC
  - Summer Site Mentor: Albes Gaona DOE-HQ EM-13
  - “Climate Change Vulnerability Assessment and Adaptation Plan for DOE Sites”

Project 2: Conferences & Presentations

Proceedings of the Waste Management Symposia 2016, Phoenix, AZ, March 2016

- Professional Posters/Papers
  - R. Gudavalli, C. Pino, Y. Katsenovich, M. Denham, *"Synergetic Interactions between Uranium, Humic Acid, Silica Colloids and SRS Sediments at Variable pH".*
  - R. Gudavalli, K. Pazan, M. Denham, B. Looney, *"Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems at F/H Area at Savannah River Site".*
  - M. Mahmoudi, A. Lawrence, S. Setegn, N. Duque, B. Looney, *"Development of an Integrated Hydrological Model for Simulation of Surface Runoff and Stream Flow in Tims Branch Watershed".*
  - A. Lawrence, M. Mahmoudi, S. Setegn, N. Duque, A. Rana, B. Looney, *"Using GIS for Processing, Analysis and Visualization of Hydrological Model Data"*.
- Professional Papers/Presentations
  - S. Herrera-Landaez, V. Anagnostopoulos, Y. Katsenovich, B. Lee, M. Lee, *"The Effect of Bicarbonate on Autunite Dissolution in the Presence of Shewanella oneidensis under Oxygen Restricted Conditions".*
  - R. Lapierre, Y. Katsenovich, L. Lagos, "*Characterization of U(VI)-Bearing Precipitates Produced by Ammonia Gas Injection Technology into Unsaturated Sediments*".

Project 2: Conferences & Presentations

Proceedings of the Waste Management Symposia 2016, Phoenix, AZ, March 2016

- Student Posters
  - A. Hernandez, "*Kinetic and Mechanistic Studies of U(VI) Bearing Groundwater Treated with Sodium Silicate at the Savannah River Site*".
  - A. Rana, *"Application of Geospatial Tools to Support Development of a Hydrological Model of the Tims Branch Watershed in Aiken, SC"*.
  - C. Strand, *"Topographic Analysis to Support the Hydrology Model of the Tims Branch Watershed, Aiken, SC"*.
  - C. Wipfli, "*A Study of Sodium Silicate Treatment for the U(VI) - Impacted Acidic Groundwater at Savannah River Site's F/H area*".
  - H. Gonzalez, "*Study of an Unrefined Humate Solution as a Possible Remediation for Groundwater Contamination at SRS".*
  - N. Duque, M. Mahmoudi, *"Development of a Flow Model to Simulate Discharge in Tims Branch, Savannah River Site".*
  - R. Lapierre, "*The Characterization of Uranium Phases Produced by the NH_3 Injection Remediation Method under Hanford 200 Area Conditions".*
  - S. Di Pietro, "*Ammonia Gas Injection for Remediation of Uranium Contamination*".
  - Y. Rotterman, *"Green & Sustainable Remediation Analysis of a Packed Tower Air Stripper Used to Remediate Groundwater Contaminated with CVOCs"*.
- Silvina Di Pietro- (PhD Chemistry) DOE Fellow student, was awarded with the Roy G. Post Foundation Scholarship.
- Ravi Gudavalli won best poster award for Track 7: Environmental Remediation.
- 9 DOE Fellows presented posters based on the research conducted under this project for the WM student poster competition.

Project 2: Conferences & Presentations

- **Proceedings of the 2015 American Geophysical Union (AGU) Fall Meeting, San Francisco, CA, December 2015**
  - M. Mahmoudi, S. Setegn, A. Lawrence, N. Duque*," Integrated Modeling System for Analysis of Watershed Water Balance: A Case Study in the Tims Branch Watershed, Aiken, South Carolina."*
  - A. Lawrence, M. Mahmoudi, S. Setegn, N. Duque*, "GIS as an Integration Tool for Hydrologic Modeling: Spatial Data Management, Analysis and Visualization".*
- **ACS conference, August 2016**
  - H. Emerson, S. DiPietro, Y. Katsenovich, "*Investigation of $NH_3(g)$ treatment for the immobilization of uranium in the presence of pure minerals*". (Submitted).
  - V. Anagnostopoulos, A. Hernandez, C. Wipfli, Y. Katsenovich, M. Denham, "*Sodium silicate treatment to attenuate uranium mobility in the acidic groundwater plumes*". (Submitted).
- **Life Sciences South Florida STEM Undergraduate Research Symposium April 2nd 2016**
  - A. Hernandez, V. Anagnostopoulos, Y. Katsenovich, "*Kinetic and Mechanism Studies of U(VI) Bearing Groundwater Treated with Sodium Silicate at the Savannah River Site*".
  - A. Smoot, R. Gudavalli, Y. Katsenovich, "*Study of Synergetic Interactions between Uranium, Humic Acid, Silica Colloids and SRS Sediments at Variable pH*".
  - S. Bird, R. Gudavalli, "*Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems at F/H Area at Savannah River Site*".
  - Alex Hernandez won the first place in the poster competition.
- **Christine Wipfli (DOE Fellow) won the International Atomic Energy Agency (IAEA) internship; left last week to start her one year internship in Vienna, Austria.**

Project 2: Publications

- Yelena Katsenovich, Claudia Cardona, Robert Lapierre, Jim Szecsody, Leonel Lagos, 2016. *The Effect of Si and Al Concentrations on the Removal of U(VI) in the Alkaline Conditions Created by NH_3 Gas (Submitted to Applied Geochemistry Journal).*

FLORIDA INTERNATIONAL UNIVERSITY

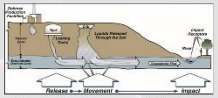
The Characterization of Uranium Phases Produced by the NH_3 Injection Remediation Method Under Hanford 200 Area Conditions

FIU Applied Research Center

Robert Lapierre (DOE Fellow; Graduate Student – Chemistry) - Applied Research Center, Florida International University

Background

Improper discharge and failed storage tanks have resulted in the contamination of the Hanford vadose zone with radiologically contaminated waste



Remediation methods considered for the area include sequestration of uranium by injection of ammonia (NH_3) gas

- Increases the pore water pH, promoting the dissolution of soil minerals
- Re-establishment of natural conditions is believed to cause the recrystallization of minerals and the co-precipitation of uranium phases

Objectives & Significance

Characterization of the precipitates formed when the ammonia (NH_3) injection method is applied to synthetic pore water on a laboratory scale. This involves:

- Identification of the uranium-bearing phases
- Study of the impact of major pore water constituents

This study will supplement the ongoing research into the application of the NH_3 remediation method to the Hanford vadose zone uranium contamination while working to broaden the understanding of the roles constituents play in the subsurface remediation technology

Sample Preparation & Analysis

Synthetic pore water solutions were prepared to mimic selected major constituents of the pore water from the Hanford 200 Area

- Varying concentrations of calcium and carbonate in solutions will be used to evaluate effects
- Prior results led to method modifications such as
  1. Preparation of duplicate (Group B) samples
  2. Vacuum filtration of all samples
  3. DI-water rinse of duplicate samples (5 mL)

Samples were subject to NH_3 gas treatment to pH 11-12 and allowed to re-establish pre-treatment pH before vacuum filtration to isolate solid and liquid phases for analysis

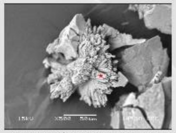
Ammonia gas injection and vacuum filtration steps of the modified sample preparation

Precipitate and supernatant were analyzed by scanning electron microscope with energy dispersive spectroscopy (SEM/EDS) and kinetic phosphorescence analyzer (KPA), respectively

Results

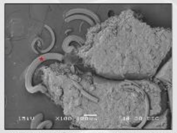
Precipitate Analysis

Scanning electron microscopy showed eye-catching structures likely to be mineralogically significant though EDS analysis revealed no significant uranium content.



Element	Wt%	At%
C K_α	18.43	28.04
N K_α	03.11	04.05
O K_α	46.75	53.41
Na K_α	00.73	00.58
Al K_α	00.08	00.06
Si K_α	00.19	00.13
U M_α	00.70	00.05
Ca K_α	30.01	13.69

SEM image w/ EDS data for specimen 25-05A, prepared using a 25mM of HCO_3^-, 5mM Ca^{2+}, and 200ppm uranium pore water solution

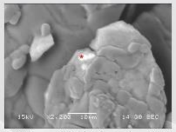


Element	Wt%	At%
C K_α	03.30	04.87
N K_α	16.02	20.08
O K_α	42.34	46.46
Na K_α	36.79	28.10
Al K_α	00.26	00.17
Si K_α	00.35	00.22
U M_α	00.72	00.05
Ca K_α	00.21	00.09

SEM image w/ EDS data for specimen 50-00A, prepared using a 50mM of HCO_3^- and 200ppm uranium pore water solution

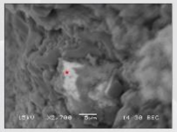
- EDS analysis suggests that these are likely calcium carbonate ($CaCO_3$) (left) or nitratine ($NaNO_3$) (right), two precipitates expected based on composition and X-ray diffraction analysis of previous samples

Continued SEM analysis revealed areas of high average atomic weight which were then confirmed to be uranium-rich by EDS analysis



Element	Wt%	At%
C K_α	06.33	11.22
N K_α	03.61	05.48
O K_α	41.41	55.08
Na K_α	06.60	06.11
Al K_α	01.78	01.40
Si K_α	25.58	19.38
U M_α	14.69	01.31

SEM image w/ EDS data for specimen 50-00A, prepared using a 50mM of HCO_3^- and 200ppm uranium pore water solution



Element	Wt%	At%
C K_α	06.96	12.37
N K_α	04.68	07.13
O K_α	39.29	52.44
Na K_α	11.00	10.22
Al K_α	01.59	01.26
Cl K_α	00.91	00.55
Si K_α	19.05	14.48
U M_α	16.40	01.47
Ca K_α	00.12	00.06

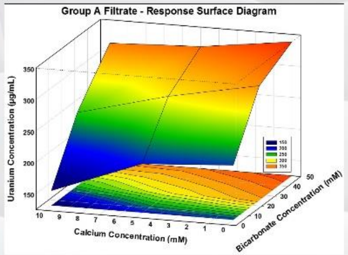
SEM image w/ EDS data for specimen 50-05A, prepared using a 50mM of HCO_3^-, 5mM Ca^{2+}, and 200ppm uranium pore water solution

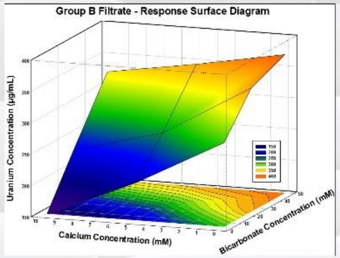
- These uranium phases were exclusively found in the non-rinsed (Group A), high bicarbonate samples

Supernatant Analysis

The kinetic phosphorescence analyzer results were used to determine the concentration of uranium retained in the supernatant filtrates and, by difference, precipitated in the solid phase

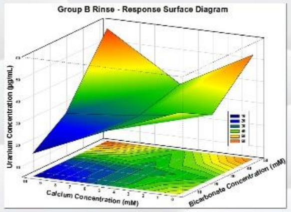
- Resulting data was used to prepare response surface diagrams, allowing for the visualization of the relationship between initial calcium and bicarbonate content and the retention of uranium in the aqueous solution.





The diagrams display clear trends between uranium retained and initial pore water solution component concentrations

- High bicarbonate is associated with high uranium concentrations
- High calcium content is associated with low uranium concentrations



The response surface diagram for the filtered DI-water rinse resulted in concentrations an order or magnitude less than the filtered supernatant

- The rinse filtrates break from the trend established by the sample filtrates
- Similar to previous groups, the high calcium, low bicarbonate shows the lowest uranium retained in solution

Conclusions

With the exception of low bicarbonate samples, the structures suspected to be calcium carbonate were detected in nearly all calcium containing specimen, regardless of a rinsing step

The uranium rich solid phases detected by SEM/EDS were morphologically significantly different compared to the distinct phases observed in previous samples

ie:

SEM images of uranium rich regions from prior 200ppm (L) and 500 ppm (R) samples

Analysis of the filtered supernatant solutions revealed that the concentration of uranium retained in solution after treatment was maximized with increased bicarbonate concentration and minimized by increased calcium content

- The high concentration of retained uranium in the low calcium, high bicarbonate supernatant solutions is undermined by the consistent identification of solid uranium phases by EDS analysis
- Similarly the data implies that the low bicarbonate, high calcium precipitates should contain the most solid uranium phases due to the low uranium concentrations retained in supernatants.
  - ➢ SEM/EDS analysis contradicts this implication due to the lack of any significant presence of uranium in the solid phase

Future Work

Electron microprobe will be used to analyze the elemental content uranium phases observed by SEM/EDS

- Samples will be mounted in epoxy prior to grinding and polishing with assistance from an appropriate facility

X-ray diffraction and transmission electron analysis will be used to attempt to determine a diffraction pattern for the crystalline uranium forms

Sequential extractions of sample precipitates will be used to characterize the uranium phases present based on solvent interactions

Acknowledgements

- Dr. Yelena Katsenovich (FIU-ARC)
- Dr. Yong Cai (FIU-Chemistry)
- Dr. Leonel Lagos (FIU-ARC)
- Dr. Jim Szecsody (PNNL)
- DOE-FIU Science and Technology Workforce Development Program

Advancing the research and academic mission of Florida International University.

A Comparison of NH_4OH and NaOH Treatments for Uranium Immobilization in the Presence of Kaolinite

Silvina Di Pietro – DOE Fellow
Dr. Hilary Emerson and Dr. Yelena Katsenovich – Mentors
Florida International University

FIU Applied Research Center

Background

The DOE Hanford Site in Washington State has deposited over 200,000 kg of uranium (U) in the vadose zone. This is legacy contamination from the production of plutonium during the Cold War. In addition, U is a major risk driver at the site due to the large release and its high mobility in the groundwater. Its increased mobility is due to the site's oxidizing conditions and the presence of carbonate creating mobile species [K_d at pH 8 (0.11 – 4 L/kg)] (Zachara *et al.*, 2007).

However, the remediation of U is further complicated by the deep vadose zone. This zone is ~270 feet deep, consisting largely of quartz and aluminosilicate clays. Remediation approach requires a method that would reduce uranium mobility and its downward migration to the groundwater without addition of liquid amendments.

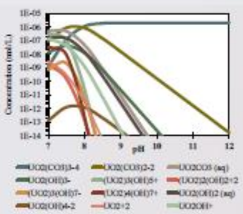


Figure 1. Aqueous speciation for 500 ppb U in 0.007 M NaCl and 0.00038 atm CO_2

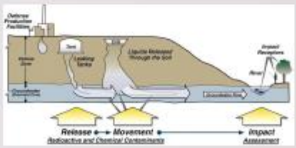


Figure 2. Schematic diagram of waste discharges to the Hanford Site vadose zone
(Gee *et al.*, 2007)

Ammonia Gas Injection Technique

$$NH_{3(aqu)} + H_2O_{(l)} \leftrightarrow NH_4{}^+{}_{(aqu)} + OH^-{}_{(aqu)}$$
K_a=1.82x10^{-5}

$$NH_{3(aqu)} \leftrightarrow NH_{3(g)}$$
KH=0.016 atm/mol

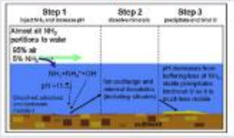


Figure 3. Process that occurs with injection of ammonia vapor into unsaturated sediments
(Zhong *et al.*, 2015)

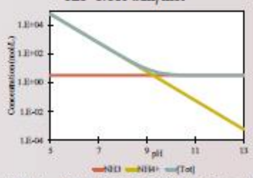


Figure 4. Ammonia solubility in 5% NH_3 gas

Project Objective

To understand NH_3 gas injection for remediation of uranium in the vadose zone at the Hanford Site. To establish a baseline, this technology is being compared to NaOH injection.

- To understand equilibrium U removal from the aqueous phase [adsorption and (co)precipitation]
- To determine the fate of NH_3 gas in the vadose zone

Batch Experimental Protocol

Initial Equilibrium Partitioning of U

1. Six initial samples prepared at pH ~7.5, ionic strength solution (3.2 mM NaCl or synthetic porewater) and mineral (kaolinite - 5 g/L) with 40 mL total volume
2. Adjusted to pH prior to addition of U(VI)$O_2{}^{2+}$ at 500 ppb [Ricca Chemical]
3. Monitored for ~3 days to ensure that equilibrium was reached
4. Aliquot was then centrifuged and spun to remove solids > 120 nm
5. Aqueous phase analyzed by KPA (U), ICP-OES (Al and Si), ammonia gas-sensing electrode (total $NH_3/NH_4{}^+$)

Equilibrium Partitioning of U following injection of NH_3 or NaOH

1. Samples adjusted to pH ~11.5
   - Samples 1-3 adjusted by 2.5 M NaCl + 0.025 M NaOH
   - Samples 4-6 adjusted by 2.5 M NH4OH
2. Monitored for ~3 days to ensure that equilibrium was reached
3. Aliquot centrifuged and spun to remove solids >120 nm
4. Aqueous phase analyzed by KPA (U), ICP-OES (Al and Si), ammonia gas-sensing electrode (total $NH_3/NH_4{}^+$)

Table 1. Synthetic Porewater Constituents

Salts	Conc (mmol/L)	Ionic Strength (mmol/L)
$KHCO_3$	0.22	0.22
$NaHCO_3$	1.10	1.10
$CaCl_2$	1.40	4.19
$MgCl_2$	0.57	1.70
total	3.28	7.20

Figure 5. Shaker rotator equilibrating samples at 120 rpm

Figure 6. Kaolinite mineral $[Al_2Si_2O_5(OH)_4]$

Figure 7. Centrifugation step with *ThermoScientific* centrifuge to remove particles >120 nm, 5000 rpm for 30 min

Data is presented below as a K_d (mL/g):

$$K_d = \text{partitioning coefficient} = \frac{\text{solid conc.}}{\text{aqueous conc.}}$$

K_d >> will be immobile, K_d << will be mobile

Note: In this system, we are using an "apparent" K_d as it represents multiple processes (i.e., precipitation, sorption and complexation).

Results and Discussion

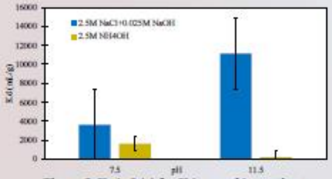


Figure 8. K_d (mL/g) for U (500 ppb) sorption to kaolinite (5 g/L) in 0.007 M NaCl solution using either 2.5 M NH_4OH (yellow) or 0.025 M NaOH + 2.5 M NaCl (blue)

A significant increase occurs in the partitioning coefficient when adjusting pH using NaOH + NaCl versus NH_4OH in NaCl background electrolyte.

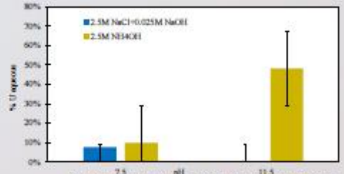


Figure 9. Aqueous fraction of U (500 ppb) with respect to pH for kaolinite (5 g/L) suspensions in NaCl solution with pH adjusted up with either 2.5 M NH_4OH (yellow) or 0.025 M NaOH + 2.5 M NaCl (blue)

The aqueous fraction of U increases as pH increases due to repulsive forces with kaolinite's negative surface and negative/neutral U species in NaCl background electrolyte.

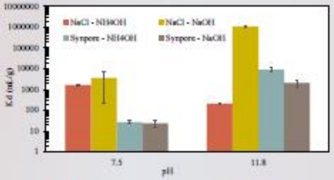


Figure 10. Comparison of U partitioning between NaCl and synthetic porewater background electrolyte at similar total ionic strength

In synthetic porewater, removal of U from the aqueous phase increases with pH as shown by the increased partitioning coefficient.

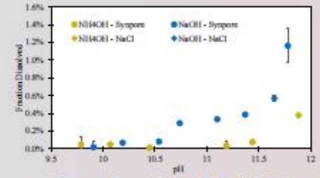


Figure 11. Comparison of Si dissolution from kaolinite (5 g/L) in either synthetic porewater or NaCl with pH adjustment by either NaOH (blue) or NH_4OH (yellow)

Dissolution of Al & Si containing minerals at high pH can potentially allow for U to co-precipitate .

Conclusions

- At pH ~7.5 significantly greater sorption occurs for NaCl as compared to synthetic porewater due to greater formation of U-carbonate species in synthetic porewater [Figure 8]
- At pH ~11.5 in NaCl, aqueous U in NH_4OH solution increases due to desorption from kaolinite as neutral or negative U-carbonate species form [Figure 9]
- At pH ~11.5 in synthetic porewater, significant removal of U occurs with both treatments but is higher of NH_4OH possibly due to a decrease in solubility due effect of molecular species on solubility (i.e. NH_3) [Figure 10]
- Significant dissolution of kaolinite occurs at elevated pH and Si and Al may co-precipitate with U species [Figure 11] It is likely that co-precipitation occurs at elevated pH for synthetic porewater but is also expected to occur as pH decreases as NH_4OH evaporates in NaCl system leading to oversaturation of Al/Si.

Significance for Remediation:

- Ammonia gas injection may be an effective remediation technique for U in the Hanford vadose zone due to its significant removal of U from the aqueous phase (~10^4 mL/g compared to 10^{-1} to 10^0 mL/g in natural conditions)
- As ammonia evaporates, pH returns to neutral allowing for U-aluminosilicate complexes precipitates. If (co)precipitation occurs, then U mobility decreases
- Ammonia gas will not increase the liquid flux to the groundwater

Future Work

- Batch experiments for additional minerals and sediments (illite, montmorillonite, quartz, muscovite and natural sediments relevant to Hanford 200 Area)
- Sequential extractions to understand the lability of sorbed and co-precipitated U species
- Speciation modeling of the aqueous U
- Mineral and sediments characterization (XRD, BET, SEM + EDS)
- Kinetic batch experiments

Acknowledgements

DOE-FIU Science & Technology Workforce Development Program and Dr. Leonel Lagos – Director of Research, Applied Research Center

FLORIDA INTERNATIONAL UNIVERSITY

Kinetic and Mechanism Studies of U(VI) Bearing Groundwater Treated with Sodium Silicate at the Savannah River Site

Alejandro Hernandez- DOE Fellow, Mentors: Dr. Yelena Katsenovich and Dr. Vasileios Anagnostopoulos

FIU Applied Research Center

Background

- The Savannah River Site (SRS) was one of the most significant sites for the production of materials related to the U.S. nuclear program during the early 1950s to late 1980s.
- An estimated 36 metric tons of plutonium were produced, and 3.4 billion gallons of hazardous waste solution were received in the F and H areas.
- The constituents of concern (COCs) associated with the F and H Area HWMF groundwater plume are uranium-238, tritium, iodine-129, strontium-90, curium-244, americium-241, technetium-99, cadmium, and aluminum, and mercury.

Objectives

1. Explore the application of sodium silicate for the restoration of the alkalinity of the treatment zone.
2. Investigate the immobilization of COCs, concentrating on U(VI).
3. Elucidate the sorption properties of U(VI) on SRS soil at circumneutral conditions, through kinetic and mechanistic studies.

Materials and Methodology

Sorption experiment

- Batch experiments were conducted bringing in contact:

3 Different SRS Soil Fraction		
d<63 µm	63µm<d<180µm	180µm<d<2mm
2 Synthetic Mixtures		
Quartz	95 % Quartz and 5 % Kaolinite	

- With SRS synthetic ground water containing 500 ppb U(VI), amended with sodium silicate to circumneutral conditions (pH~6.5).

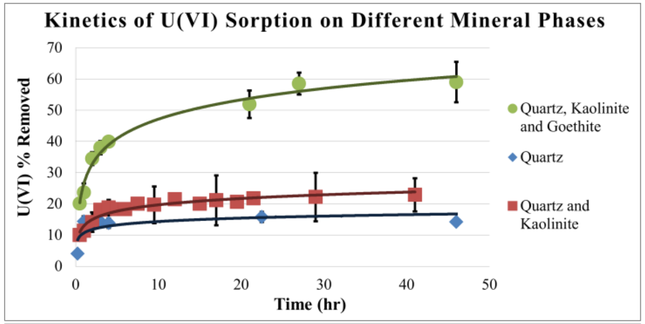
Desorption experiments

- Supernatant was removed from

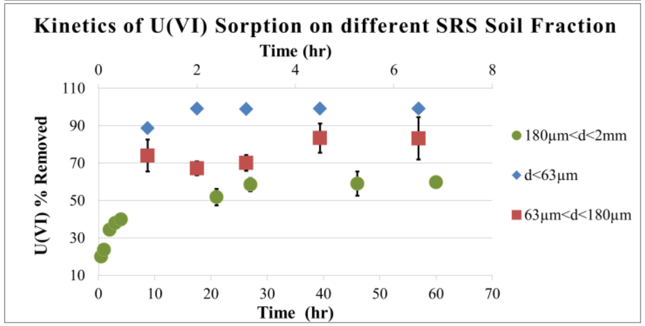
2 synthetic mixtures	
Quartz	95 % Quartz and 5 % Kaolinite
SRS Soil Fraction	
180µm<d<2mm	

- SRS synthetic ground water was reintroduced, and left to equilibrate for 26 hours.
- U(VI) analysis of all samples was performed through Kinetic Phosphorescence Analysis (KPA).
- Solid: Liquid ratio was kept constant throughout the experiments and equal to 20:1 and all experiments were performed in triplicates.

Results



Desorption	
Quartz, Kaolinite and Goethite	50%
Quartz and Kaolinite	100%
Quartz	100%



SRS Soil Fraction	U(VI)% Removed	[Fe] in the Soil (mg/g)
d<63 µm	100 %	89.1
63µm<d<180µm	80 %	70.2
180µm<d<2mm	60 %	40.0

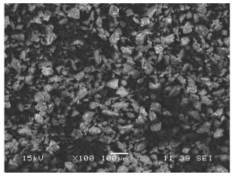


Figure 1 SRS Soil Fraction: d<63 µm

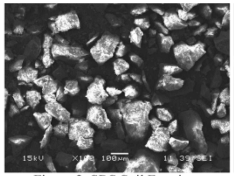


Figure 2. SRS Soil Fraction: 63µm<d<180µm

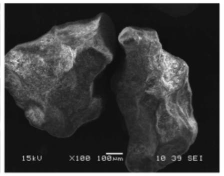


Figure 3. SRS Soil Fraction: 180µm<d<2mm

Advantages & Considerations

- ✓ Alkalinity restoration using a **cost-effective** & **environmentally benign** technology.
- ✓ Provides greater insight on the geochemical interactions of U(VI) with SRS soil.

Conclusions

- Goethite (iron bearing oxyhydroxide mineral) is proportional to the [Fe] in the soil.
- Goethite is the most reactive mineral phase of SRS soil involved in U(VI) retention.
- U(VI) is strongly retained by goethite.
- Positive correlation between the iron concentration in the soil and U(VI) sorption.

ACKNOWLEDGMENTS

Dr. Yelena Katsenovich
Dr. Vasileios Anagnostopoulos
Dr. Ravi Gudavalli
Dr. Leonel Lagos
FIU - Applied Research Center
Savannah River National Lab
DOE-FIU Science & Technology Workforce Development Program

This research was supported by the U.S. Department of Energy Office Of Environmental Management - Office of Science and Technology.

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Advancing the research and academic mission of Florida International University.

Sodium Silicate Treatment for Uranium (VI) Bearing Groundwater at F/H Area at Savannah River Site

Christine Wipfli – Department of Energy Fellow, Florida International University

FIU
Applied Research Center

Background

- The Savannah River Site (SRS) was one of the most significant manufacturing facilities during the Cold War era for the research and development of nuclear weapons and materials.
- As a result of six decades of hazardous waste management and storage, the groundwater at the F/H Area Seepage Basins at SRS was impacted by the disposal of approximately 1.8 billion gallons of radioactive and hazardous waste.
- At the end of the Cold War, the Site's mission changed to support the environmental restoration of the Site by remediating contaminated soil and groundwater .
- This research focuses on controlling the mobilization of uranium (VI) in the acidic groundwater plumes at the SRS F/H Area Seepage Basin by introducing sodium silicate, an alkaline solution.

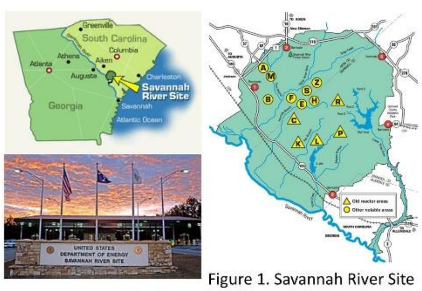

Figure 1. Savannah River Site

Objectives

- Restore pH levels of the treatment zone to circumneutral conditions by the addition of sodium silicate.
- Identify the conditions for the immobilization of U (VI) as a consequence of sodium silicate addition via a sorption process. Analyze the influential factors of this process.
- Investigate the different size particles with which U(VI) is associated, along with the composition and morphology.

Methodology & Results

Cation Influence on U(VI) Sorption

- A preliminary experiment was conducted to investigate the influence of cations present in SRS groundwater on the sodium silicate-uranium sorption process.
- Separate batch experiments were created containing 20 ml of one of the two types of water, 1) deionized water or 2) SRS synthetic groundwater, replicating the sites natural groundwater composition. Added to each sample: 500 ppb uranium(VI), 400 mg of SRS Soil, and 70 ppm sodium silicate concentration.
- The experiment revealed similar results for both water types, indicating that cations in the SRS groundwater do not influence U(VI) retention by the sediment.

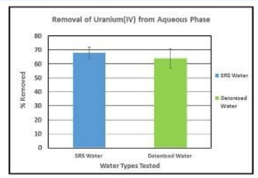

Figure 2. Percent removal of uranium (VI) from the aqueous phase for SRS synthetic groundwater, (blue) and for deionized water (green).

Analyzing U(VI) Particle Sizes via Filtration

- Sequential experiments were conducted filtering solutions (containing SRS synthetic groundwater, SRS soil, U(VI), and sodium silicate) in order to investigate the different size fractions and morphology of the particles in the solution.
- The different size fractions, divided into the average particle diameter (d) investigated were:
  d > 0.45 µm, 0.2 µm < d < 0.45 µm and d < 0.2 µm

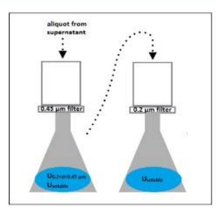

Figure 3. Experimental process showing two-step filtration method. Different U(VI) fractions were estimated using a mass-balance equation.

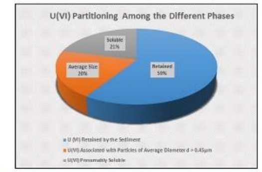

Figure 4. The distribution of the different uranium (VI) particle phases under the experimental conditions studied.

SEM/EDS Analysis of Filters

- Extractions from the filters were analyzed using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS), to gain a better understanding of the morphology and the composition of the size fractions.
- The elemental composition of the filter particles contained Si and O; also Al and Fe which contain kaolinite and goethite.
- Elemental and morphological analysis of the 0.45 µm filters are displayed below.

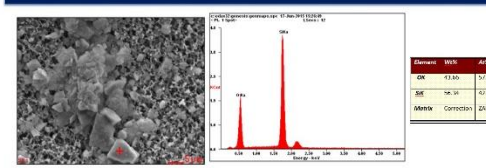

Figure 5. SEM image and EDS analysis of a particle from a 0.45µm filter.

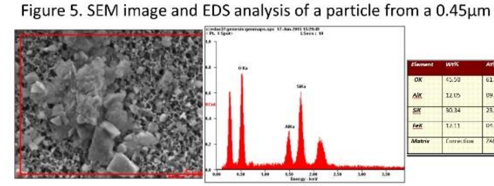

Figure 6. SEM image and EDS analysis of particles accumulated on 0.45µm filter; average elemental composition of large surface area.

Future Work

- Assess stability of sequestered uranium (VI).
- Further investigate the role of aluminum and iron leaching from SRS soil on the overall sorption process.
- Conduct continuous flow experiments via column testing to observe the removal of U(VI) from the aqueous phase.

ACKNOWLEDGEMENTS
Mentors:
Dr. Yelena Katsenovich
Dr. Vasileios Anagnostopoulos
Dr. Ravi Gudavalli
Dr. Leonel Lagos

FIU - Applied Research Center
Savannah River National Lab
DOE-FIU Science & Technology Workforce Development Program

This research was supported by the U.S. Department of Energy's Office Of Environmental Management Under Cooperative Agreement # DE-EM0000598

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Winner "BEST POSTER"
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Synergetic Interactions between Uranium, Humic Acid, Silica Colloids and SRS Sediments at Variable pH

Ravi Krishna Gudavalli *, Christian Pino *, Yelena Katsenovich *, Miles Denham **
*Applied Research Center - Florida International University, Miami, FL **Savannah River National Laboratory, Aiken, SC

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Background

- The Savannah River Site's (SRS) F/H Area seepage basins received approximately 1.8 billion gallons of acidic waste containing radionuclides and dissolved heavy metals including uranium (VI)
- Humic substances (HS) are major components of soil organic matter, divided into three fractions: humin, fulvic acid and humic acid (HA). HA is insoluble below pH 1 and soluble above pH 3
  - HA is able to influence absorption and migration behavior of heavy metals
  - HA acts as a metal complexing ligand with a high complexation capacity
  - HA is able to bind to both hydrophobic and hydrophilic materials due to structure and colloidal properties.
- Silica (SiO_2) is mainly associated with HA by weak interactions such as Van Der Waals forces but may form hydrogen bonds depending on the protonation state (Yang et al., 2013)

Objectives

- Analyze synergistic interactions between U(VI) ions, HA and colloidal silica under varying pH conditions from 3 to 8
- Study the effect of pH on component interaction and uranium removal

Methodology

- Multi-component batch systems were prepared to a total volume of 20mL per sample tube as follows:
  - Si (3.5mM) + U(VI) (0.5ppm) + HA (50ppm), no sediment
  - U(VI) (0.5ppm) + HA (50ppm), (no Si or sediment)
  - Sediment + Si (3.5mM) + U(VI) (0.5ppm) + HA (50ppm)
  - Sediment + U(VI) (0.5ppm) + HA (50ppm), (no Si)
  - Control: U(VI) (0.5ppm), (no Si, HA or sediment)
- Triplicate samples for each batch were prepared and pH of mixture then adjusted to the desired value between 3 and 8 using 0.01 M HCl and 0.1 M NaOH
- Samples are kept on a shaker platform at 100 RPM for 48 hours at room temperature; samples were centrifuged at 2700 rpm at 22°C for 30 minutes
- Filtered (through 0.45 µm PTFE syringe filter) and unfiltered aliquots were diluted for U(VI) and Si analysis via KPA and ICP-OES

Results & Discussion

Filtered Samples

- At low pH, aggregation and coagulation of the HA hydrophobic groups are the major force causing complexation of uranyl cations; at high pH, the proton-binding sites of HA molecules are sufficiently dissociated to carry any significant charge, thus reducing binding potential
- Non-sediment batches revealed a lower U(VI) removal compared to sediment-containing batches; sediment-bearing samples showed a 30% increase in uranium removal
- Colloidal silica removal remained around approximately 80%, similar through all pH values, though with a slight drop at pH 7 and 8 which contained non-sediment-bearing samples

Unfiltered Samples

- The removal of uranium in the unfiltered samples was slightly lower compared to the filtered samples; overall uranium removal decreased as pH increased
- Colloidal silica does not seem to have a significant effect on the removal of U(VI) due to U(VI) binding to silica colloids remaining in suspension; the silica may have formed semi-soluble tertiary complexes with the HA and U(VI), remaining in suspension after centrifugation

Uranium Removal; 50 ppm HA Filtered Samples				
pH	Si, HA, U	HA, U	Si, HA, U, Sediment	HA, U, Sediment
3	55.17	49.22	83.83	79.16
4	53.2	40.52	65.36	70.06
5	38.25	32.98	49.59	52.18
6	30.87	32.98	43.08	45.82
7	19.51	20.89	39.26	44.8
8	46.14	34.17	41.57	43.52

Uranium Removal; 50 ppm HA Unfiltered Samples				
pH	Si, HA, U	HA, U	Si, HA, U, Sediment	HA, U, Sediment
3	31.80	44.28	71.83	64.53
4	44.98	45.01	52.94	60.77
5	37.55	18.24	40.66	40.12
6	28.27	26.88	25.71	36.06
7	22.92	24.76	22.60	33.93
8	21.40	18.16	33.02	33.00

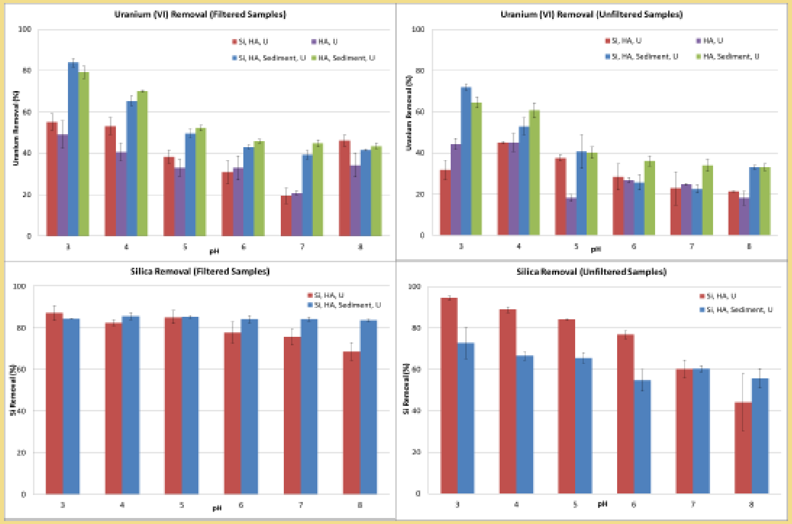

Fig. 1: Uranium and silica removal in filtered and unfiltered samples

Conclusions & Benefits

- Uranium removal is directly influenced by the presence and interactions of humic acid and sediment
  - Uranium removal at pH 3 yielded a 35% increase with the addition of sediment; as the pH reaches near neutral, the removal of uranium due to the addition of sediment decreased to 8%
- Colloidal silica played a minor role; any uranium removal was from a semi-soluble complex with silica and only removed through a 0.45 µm filter
- Provides information on
  - Whether uranium is bound to silica in the treatment zone
  - Synergic interactions between Si and humic acid on uranium removal

Acknowledgments

- Funding for this work was provided by the U.S. Department of Energy Office of Environmental Management under cooperative agreement DOE-EM0000598

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Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems at F/H Area at Savannah River Site

Ravi Gudavalli[1], Kiara Pazan [1], Miles Denham[2], Brian Looney[2]

[1] Applied Research Center, Florida International University, Miami, FL; [2]Savannah River National Laboratory, Aiken, SC

Background

- The Savannah River Site's F/H Area seepage basins received approximately 1.8 billion gallons of low level acidic waste solutions containing dissolved metals and radionuclides
- Significant quantities of uranium isotopes, iodine-129, Tc-99, and tritium migrated into the groundwater, creating an acidic plume with a pH between 3 and 5.5
- Studies have shown humate to be a potential approach for controlling mobility of contaminants as U is expected to sorb strongly onto humate-loaded sediments at mildly acidic pH
- Huma-K is an unrefined humic substance high in humic and fulvic compounds, made from leonardite, an organic-rich mineral formed due to decomposition by microorganisms

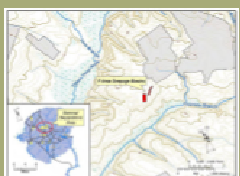


Fig. 1: F-Area seepage basins

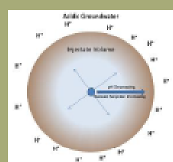


Fig. 2: Conceptual behavior of humate injected

Objectives

- To evaluate the potential use of Huma-K to enhance attenuation of uranium in the acidic F-Area aquifer
- To study the migration and distribution of Huma-K injected into subsurface systems via column experiments
- Obtain sorption and desorption parameters under different pH levels

Materials and Methods

- Soil Characterization of SRS's F-Area soil
  - Bulk Density: 1.33 g/cm^3
  - Porosity: 0.495
  - Particle Density: 2.65 g/cm^3
  - Soil pH: 4.06
- **Humate Injection Scenarios:** A Langmuir model was used to simulate and observe breakthrough curves to determine optimal Huma-K concentration and flow rate

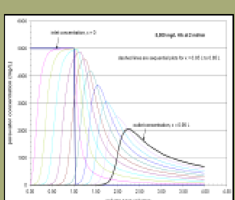


Fig. 3: Huma-K injection scenario at 5,000 ppm at 2 mL/min

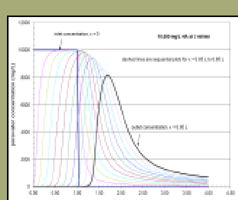


Fig. 4: Huma-K injection scenario at 10,000 ppm at 2 mL/min

Results and Discussion

Bromide Tracer Tests:

- A conservative bromide tracer was injected to determine the column's pore volume (PV) and transport parameters

Table 1. Results from Bromide Tracer Injections

Column	Recovery (%)	PV (mL)	Variance, σ^2	P_e	Retardation Factor	K_d (L/kg)
1	98.2559	85.80	107.24	33.3	1.35	0.13
2	100.511	74.12	63.34	42.35	1.46	0.17

Fig. 5: Teflon adaptor

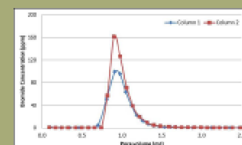


Fig. 6: Bromide concentration profile

Sorption/ Desorption of Huma-K:

- 1 PV of 5000 ppm of Huma-K with adjusted pH 9 was injected into preconditioned columns of pH 3.5 and 5, followed by 4 PV of artificial groundwater (AGW)
  - Effluent samples were collected at regular intervals and HA concentrations were measured using a UV-VIS spectrophotometer

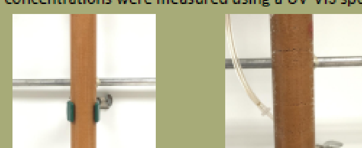


Fig. 7: Soil pre and post Huma-K loading

- Breakthrough curves show most humate injected was retained until after 1.5 PV of AGW, where concentration peaked at 6000 ppm and 5700 ppm for Columns 1 and 2, respectively (Fig. 7)
  - A possible explanation is the precipitation/re-dissolution of humate as it moves through the column

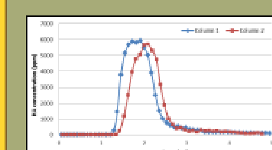


Fig. 7: Breakthrough curve of HA concentration in the column effluent

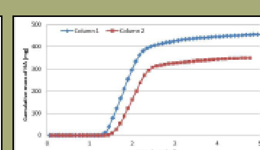


Fig. 8: Cumulative mass of humic acid collected

Results and Discussion (Cont.)

- Column 1 had a stronger pH gradient. After initial injection, pH is low and humate has precipitated and significantly sorbed. As AGW flows through, it dissolves precipitated HA and desorbs HA. Thus, there is higher concentration of HA eluting from Column 2 than Column 1 in 2nd PV.
- The high 5000 ppm HA concentration may have the buffering capacity to bind more protons in solution and raise pH faster for Column 1 because of the strong pH gradient

Table 2. Retention of Humic Acid

Column	pH		Humic Acid		
	Initial	Final	Injected (mg)	Recovered (mg)	Retained (mg)
1	3.72	6.46	576.03	457.14	118.89
2	4.77	7.08	521.52	350.06	171.46

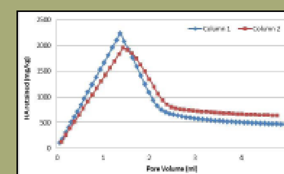


Fig. 9: Retention of HA in columns

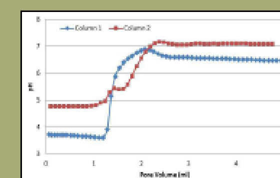


Fig. 10: Change in pH of the columns

Benefits

- Understand the sorption of humic acid onto SRS sediments and its effectiveness on uranium mobility in the subsurface
- The research will provide coupling between flow and transport of the contaminant in the subsurface and will investigate the spatial and temporal changes within the subsurface to simulate the response of the system after injection of humate.

Conclusions

- Overall, more HA was retained in column 2, which was preconditioned with a pH 5 AGW solution, than in column 1, which had pH 3.5. The increase in pH increased in the retention of HA by 180 mg per kg of soil. The results were different than expected due to the unanticipated effects of precipitation and dissolution because of mechanical and physicochemical factors.

Future Work

- Perform total organic carbon (TOC) analysis for sediments from columns to estimate the distribution of Huma-K.
- Inject uranium into the soil columns to study the effect of sorbed humic acid on the mobility of uranium through porous media.

Acknowledgements

- This research is sponsored by the U.S. Department of Energy Office of Environmental Management under cooperative agreement # DOE-EM0000598.

Advancing the research and academic mission of Florida International University.

FLORIDA INTERNATIONAL UNIVERSITY

Study of an Unrefined Humate Solution as a Possible Remediation Method for Groundwater Contamination

Hansell Gonzalez Raymat - DOE Fellow

FIU Applied Research Center

Background

Savannah River Site (SRS) was one of the major nuclear processing facilities in the U.S. where plutonium was produced during the Cold War.

Approximately 1.8 billion gallons of low level acidic waste solution containing radionuclides and dissolved metals were discharged to a series of unlined seepage basins at the F/H Area.

Uranium is a key contaminant of concern in the basin's groundwater. It is migrating into the groundwater creating an acidic plume with a pH between 3-5.5.

Huma-K

Huma-K is an organic fertilizer that comes from the alkaline extraction of leonardite (a low-rank coal).

It has a high content of humic substances which consist of complex organic compounds formed by the decomposition of plant and animal tissue.

Figure 1. Huma-K

Project Objective

The objective of this study is to provide a detailed characterization of SRS sediments and Huma-K by using Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, and Potentiometric Titrations.

This information will allow a better understanding of the interactions between Huma-K and SRS sediments.

Experimental Procedure

Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM/EDS)

(SEM/EDS) was used to investigate the surface morphology and elemental composition of SRS sediments from the F-Area and Huma-K.

A JOEL-5910-LV equipped with secondary and backscattered electron was used for the SEM analysis. EDS analysis was produced using an EDAX Sapphire detector with UTW Window controlled through Genesis software.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was used for the identification of functional groups present in Huma-K and SRS sediments (63μm fraction)

The FTIR measurements were performed using a Perkin Elmer Spectrum 100 FT-IR Spectrometer coupled with an Attenuated Total Reflectance (ATR). The spectrum of samples were collected from 4000 to 600 cm^{-1} with a spectral resolution of 4 cm^{-1}. The spectra were recorded in transmittance mode with 4 scans.

Potentiometric Titrations

Potentiometric Titrations of Huma-K and SRS sediments were performed to investigate their acido-basic properties. The experimental design is explained below:

- A certain amount of material was suspended in an electrolyte solution under an inert atmosphere with constant magnetic stirring.
- The pH was raised to 11, and once the pH of the solution stabilized, the suspension was titrated by adding small aliquots of standard HNO_3 solution (0.01 M), with the pH value recorded after each addition.
- The supernatant of the soil suspensions was collected by vacuum filtration, and a similar titrating procedure was followed.
- The net surface H^+ consumption was calculated at each pH value subtracting the H^+ supernatant consumption (second titration) from the total H^+ consumption (first titration).

Results and Discussion

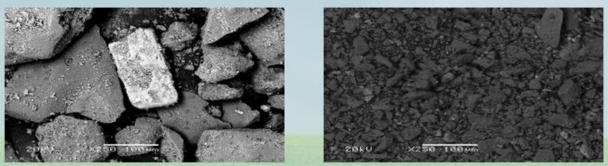


Figure 2. SEM of SRS Sediments coarse fraction (left image) and fine fraction (right image)

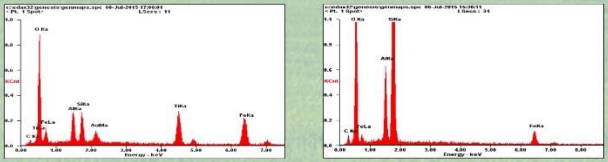


Figure 3. EDS results of SRS Sediments coarse fraction (left image) and fine fraction (right image)

The coarse (<2mm) and fine fraction s(<63μm) of SRS sediments exhibit different morphology as revealed by SEM images. EDS analysis revealed that both fractions comprise mostly of Si, Al, and Fe, which can be traced back to quartz, kaolinite, and goethite minerals present in SRS sediment. Nevertheless , Ti was also detected in the coarse fraction which can be attributed to a small percentage of titanium oxide (TiO_2), also present in SRS sediments.

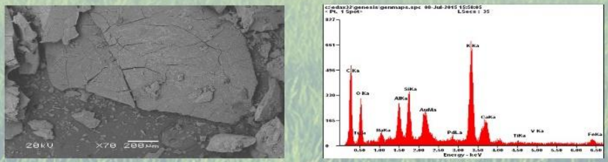


Figure 4. SEM of Huma-K (left image) and EDS analysis (right image)

SEM/EDS studies for Huma-K showed that K, C, O, Si, Ca, and Al are the main components of the sample. The presence of K is derived from the treatment of leonardite with KOH in order to extract the humic substances. Carbon and oxygen are related to the various functional groups present in the humic substances. Si, Al, and Ca come from the impurities present in Leonardite's composition.

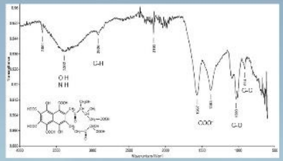


Figure 5. FTIR of Huma-K

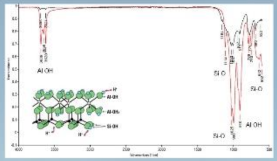


Figure 6. FTIR of SRS Sediments (fine fraction) and Kaolinite

For the Huma-K: the peaks at 3600-3000 (O-H and N-H), 2926 ($-CH_3$ and $=CH_2$), 1567-1383 (COO^-), and 1030-914 (C-O and C-C) indicate the presence of functional groups such as phenols, carboxyl, amine, and aromatic rings.

For the SRS sediments: the peaks at 3696-3621 (inner surface OH stretching), 1030-1007 (Si-O stretching), and 913 (inner surface OH bending) indicate the presence of kaolinite. The peak at 693 (Si-O bending) indicates the presence of quartz.

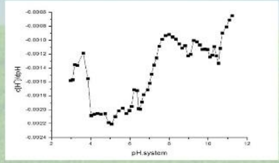


Figure 7. Potentiometric Titration of Huma-K

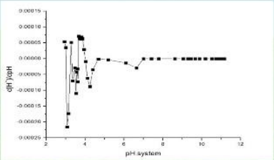


Figure 8. Potentiometric Titration of SRS sediments

The potentiometric titration results of Huma-K revealed a broad peak between pH values 4 and 6. This can be attributed to the presence of carboxyl groups arranged in different configurations, that have similar *pK* values.

The potentiometric titration curve of SRS sediments revealed reverse peaks only in the region between pH 3-4, which can be attributed to the acido-basic properties of quartz and more specifically, Si-OH groups.

Conclusion

EDS analysis, FTIR, and potentiometric titrations clearly revealed the presence of humic substances in Huma-K.
EDS and FTIR confirmed the presence of kaolinite in the fine fraction of SRS sediments.
Potentiometric titrations indicate that sediments have similar acido-basic properties as quartz mineral.

Acknowledgements

FIU Applied Research Center
- Dr. Vasileios Anagnostopoulos
- Dr. Yelena Katsenovich (mentor)
- Dr. Leonel Lagos

Savannah River National Laboratory (SRNL)
- Dr. Miles Denham
- Dr. Brian Looney

DOE-FIU Science and Technology Workforce Development Program
This research was sponsored by the U.S. Department of Energy's Office Of Environmental Management
Under Cooperative Agreement # DE-EM0000598

Florida International University

Development of an Integrated Hydrological Model for Simulation of Surface Runoff and Stream Flow in Tims Branch Watershed

Mehrnoosh Mahmoudi[1], Angelique Lawrence[1], Shimelis Setegn[1], Natalia Duque[1] (DOE Fellow), Brian Looney[2]
[1]Applied Research Center - Florida International University, Miami, FL; [2]Savannah River National Laboratory, Aiken, SC

FIU Applied Research Center

INTRODUCTION

In the 1950's and 60's, Savannah River Site (SRS), a nuclear facility owned by Department of Energy (DOE), used millions of pounds of heavy metals, primarily mercury, and solvents such as trichloroethylene (TCE) to produce tritium and separate plutonium-239 for the nation's defense program. Principal contaminants include solvents in the groundwater and vadose zone; however contamination is also found in the surface water such as in the Tims Branch stream. Since 2003, extensive cleanup activities including the remediation of contaminated soil and groundwater, have been completed at SRS. Remediation processes included treatment or immobilization of the source of the contamination to mitigate transport through soil and groundwater and clean up or slow the movement of contaminants that have already migrated from the source. Mercury treatment at SRS started in 2007 by injection of stannous (tin) chloride into the contaminated groundwater. As a result, mercury was removed as a vapor and tin dioxide was precipitated in the sediment.

PROBLEM STATEMENT

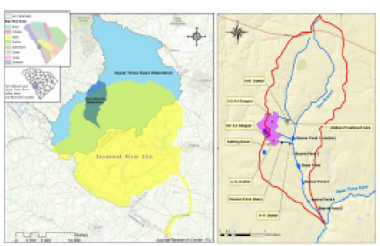
As part of mercury treatment at SRS, **stannous (tin) chloride ($SnCl_2$)** was injected into the contaminated groundwater that was passing through an air stripper. As a result, mercury was removed as a vapor and **tin dioxide (SnO_2)** was precipitated in the sediment. Tin in its elemental form is not very toxic to any kind of organism, but the **organic** form is toxic. Therefore, understanding **the fate of tin and its compounds** is of primary importance due to **their potential impact on the environment** (Donard and Weber, 1985; Maguire et al., 1986). **Tin methylation** is of great environmental concern because of its toxicity to humans and animals. Although tin is primarily deposited as sediment, **remobilization** may occur during **episodic extreme events**, such as storms or heavy rainfall. In these cases, **sediment can be resuspended in the water column** and deposited further downstream. It is therefore important to study **the fate and transport of tin** during such events, in particular its potential for methylation.

OBJECTIVES

The main objective of the research presented is to develop an integrated surface water and groundwater model to simulate water flow discharge and depth in the Tims Branch watershed during episodic extreme atmospheric events and to predict the fate and transport of tin in SRS.

STUDY AREA

SRS is one of the many nuclear facilities owned by DOE and managed and operated by Savannah River Nuclear Solutions, LLC. SRS is located in South Carolina, covers approximately 800 km^2 and is bordered on the west by the Savannah River and the state of Georgia. SRS includes facilities such as reactors, laboratories, waste disposal sites, cooling towers, incinerators, etc. **Tims Branch** is a small braided, marshy, second-order stream within SRS that starts at the northern portion of SRS and passes through Beaver Ponds 1-5 and Steed Pond, and eventually discharges into Upper Three Runs. Its drainage area is nearly 16 km^2. The length of this stream from outfall A-014 to Upper Three Runs is approximately 8 km. The average width of the stream varies between 2-3 m. Two major discharge points from SRS A/M Area into **Tims Branch** are **A014** and **A011** outfalls which are approximately 230 m apart. They combine with the main stream of Tims Branch 1,400 m from the A014 outfall. Tims Branch is a tributary of Upper Three Runs which is a tributary to Savannah River along the border of Georgia and South Carolina, and its watershed is contained within the larger Upper Three Runs watershed.



METHODOLOGY

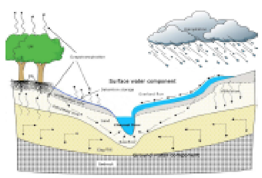
- **Conceptual Model**

A conceptual model of flow and contaminant transport was developed to understand the mechanisms involved in tin distribution.

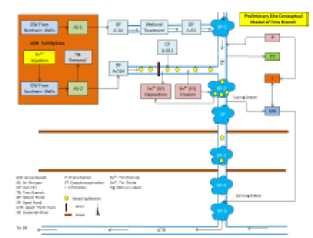
- **Hydrology Model:**

MIKE package from Danish Institute of Hydraulic (DHI) is used to simulate surface water flow in the Tims Branch watershed.

➢ *2-D Overland Flow Model: MIKE SHE*
➢ *1-D Stream Flow Model: MIKE 11*
➢ *3-D Groundwater Flow Model: SZ/UZ*



MIKE SHE Model



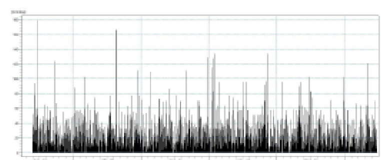
Conceptual Model

MODEL PARAMETERS

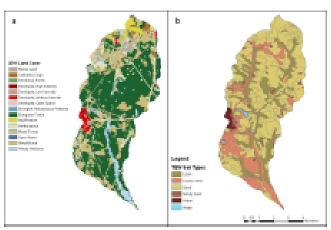
The MIKE SHE model of flow in the overland, saturated and unsaturated zones requires a number of spatial and temporal parameters which was introduced to the model in the form of standard **Geographic Information System** (GIS) data. **Topography, land cover, precipitation, geologic formation,** etc. are basic input data that is required to set up the MIKE SHE overland flow model. All geospatial data was prepared using ArcGIS and exported as GIS shapefiles for input into the MIKE model.

Land Use	Area (m^2)	%	Manning's M (1/n)
Agricultural	170,975	0.34	41
Barren Land	58,151	0.12	81
Forest	35,267,379	70.83	21
Rangeland	7,287,896	14.64	25
Urban/Built-up Land	6,816,222	13.69	90
Water	76,866	0.15	11
Wetland	115,658	0.23	23

Land use data for Tims Branch watershed



50-year record of rainfall data in SRS and Tims Branch watershed



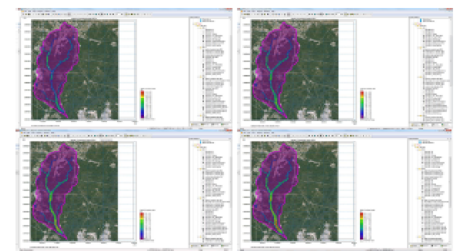
(a) 2011 geospatial distribution of land cover in TBW. Data derived from USDA National Land Cover Database (NLCD), (b) TBW soil type classification based on five dominant soil types

Vegetation ID	LAI	RD (mm)
Barren Land	1.31	4000
Cultivated Crops	3.62	1500
Deciduous Forest	5.5	2000
Developed Low Intensity	2.5	2000
Developed Medium Intensity	2.0	2000
Developed Open Space	3.0	2000
Emergent Herbaceous Wetland	6.34	2000
Evergreen Forest	5.5	1800
Hay/pasture	1.71	1500
Mixed Forest	5.5	2400
Open Water	0.0	0.0
Quarries	1.31	4000
transitional	1.31	4000
Urban/Recreational Grasses	2.0	2000
Woody Wetland	6.34	2000

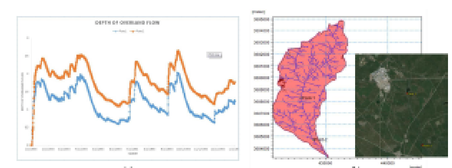
MIKE SHE vegetation data for Tims Branch watershed

PRELIMINARY RESULTS AND DISCUSSION

Preliminary simulation of overland flow was performed for a period of 40 years from January 1974 to September 2014. The figure below shows a visual illustration of the MIKE SHE model output of water elevation in Tims Branch watershed. This simplified model simulation is performed to exemplify the output results of the MIKE SHE model.



MIKE SHE seasonal water elevation simulation for Tims branch watershed



(a) Depth of overland flow in Tims Branch at two locations, (b) Point 1 near Steed Pond and Point 2 close to Upper Three Runs conjunction

The variation in the depth of overland flow in a watershed is highly dependent on rainfall intensity and distribution. The figure above also indicates that variation in the depth of overland flow highly depends on the amount and distribution of rainfall in the watershed. The simulation results are preliminary as not all of the hydrological components have been incorporated, and tend to give a general understanding of the watershed as a function of precipitation and other catchment characteristics. While the results may be considered preliminary, the model shows potential for use with future refinements in input data.

FUTURE WORK

- Coupling of the hydrology model with a contaminant fate and transport model
- Integration of the coupled hydrology/transport model with a water quality model to estimate tin distribution in Tims Branch
- Simulation of water quality under various climatic scenarios
- Sensitivity and uncertainty analyses

ACKNOWLEDGEMENTS

This research was sponsored by the U.S. Department of Energy Office of Environmental Management under Cooperative Agreement # DE-EM0000598. The authors would also like to express their gratitude to all members of the team at the Applied Research Center, Florida International University, especially DOE fellow students, Awmna Rana and Christopher Strand.

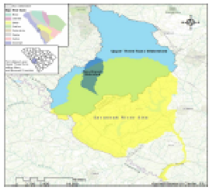
Advancing the research and academic mission of Florida International University.

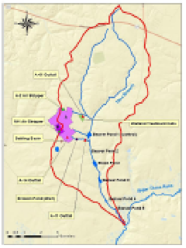
FIU Applied Research Center

Development of a Flow Model to Simulate Discharge in Tims Branch, Savannah River Site

Natalia Duque, DOE Fellow; Dr. Mehrnoosh Mahmoudi, Mentor

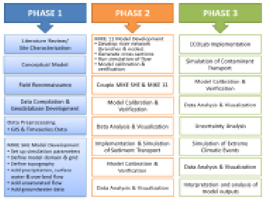
Introduction





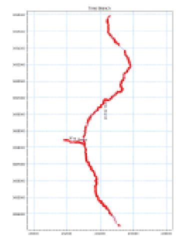
- Tims Branch Watershed (TBW) located on the Northwest side of Savannah River Site, Aiken, SC.
- Receives outflow from remediation efforts in the A/M Area.
- Tin was introduced by injection of stannous (tin) chloride into mercury contaminated groundwater.
- Tin is primarily deposited as sediment but remobilization may occur due to extreme weather events.

Project Objectives and Benefits



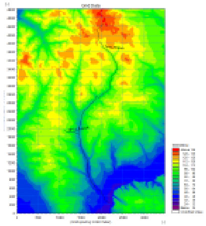
- To develop a hydrodynamic model of flow in Tims Branch using MIKE 11 software (developed by DHI).
- MIKE 11 is an implicit finite difference model that uses the one-dimensional Saint Venant equation to perform detailed modeling of surface runoff, flow, sediment transport, and water quality in rivers, channels, estuaries, and floodplains.
- MIKE 11 will be coupled with MIKE SHE and ECO Lab to develop an integrated hydrological model of Tims Branch watershed capable of simulating water flow as well as contaminant transport during extreme events such as heavy rainfall and flooding.
- Understanding the fate and transport of contaminants is of the utmost importance, especially if detrimental to human health and the environment, as in the case of tin if it becomes methylated under suitable environmental conditions.

MIKE 11 Model Setup



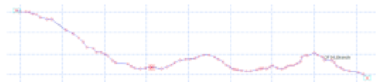
Network setup:

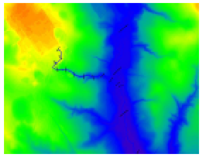
- Create points along river
- Connect points to create branches
- Define boundary conditions
- Identify hydraulic structures
- Export network data as shapefile

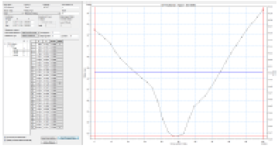


Cross-sections (using MIKE HYDRO):

- Input digital elevation model (DEM)
- Import network shapefile
- Set up MIKE HYDRO to create cross-sections automatically
- Specify water flow parameters

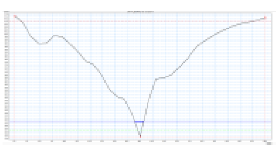


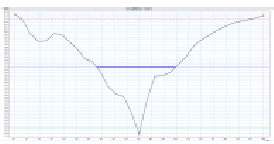


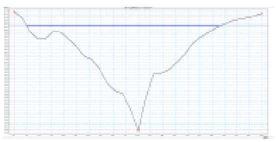


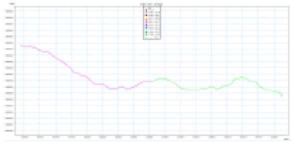
Preliminary Results

Water level animation at different times:

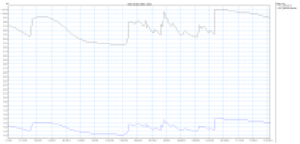




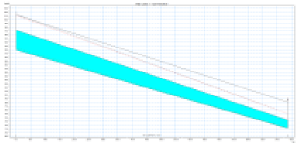




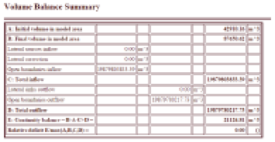
Average water level across Outfall 14 Branch



Water level timeseries at start and end points of branch

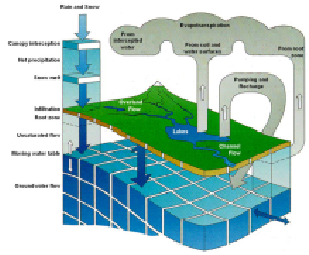


Water level profile at beginning of simulation



Water volume balance summary

Discussion



- Preliminary MIKE 11 model successfully set up.
- Model is a preliminary, simplified, simulation of river flow.
- Results analysis facilitated by powerful visualization component.
- Important water flow parameters such as Manning's coefficient are crucial for accurate results.
- When coupled with MIKE SHE, model will be able to simulate complete water cycle hydrology.
- MIKE SHE is an integrated modeling system, which couples the surface water and the groundwater processes.
- MIKE SHE is able to successfully model rivers and channels (1D), overland flow (2D), unsaturated zone flow (1D), and groundwater flow (3D).

Future Work

- Include hydraulic structures (culvert and weir)
- Model calibration and validation
- Couple with MIKE SHE
- Couple model with contaminant transport model (ECO Lab)

Acknowledgments

- Dr. Mehrnoosh Mahmoudi
- Ms. Angelique Lawrence
- FIU – Applied Research Center
- DOE-FIU Science and Technology Workforce Development Program
- Savannah River National Laboratory

This research was supported by the U.S. Department of Energy Office of Environmental Management under Cooperative Agreement # DE-EM0000598.

FLORIDA INTERNATIONAL UNIVERSITY

Topographic Analysis to Support the Hydrology Model of the Tims Branch Watershed, Aiken, SC

Christopher Strand (DOE Fellow)

FIU Applied Research Center

Background

- The United States remains adversely affected by the nuclear arms race of the Second World War. Today, facilities like the A/M area of the Savannah River Site (SRS) in South Carolina, which contained the main SRS administrative functions and manufacturing areas, are part of a long-term clean-up strategy in the U.S.
- Mercury treatment at SRS started in 2007 by injection of stannous (tin) chloride into contaminated groundwater in Tims Branch Watershed (TBW). As a result, mercury was removed as a vapor and tin dioxide was precipitated in the sediment of Tims Branch. Understanding the fate of tin and its compounds is of primary importance due to their potential impact on the environment.

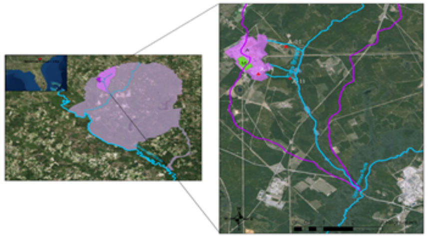


Fig 1. The A/M Area and A-014 outfall of the Savannah River Site

Objectives

- The aim of this study is to investigate the changes in ground topography that may impact the flow velocity of water discharged from the A-014 outfall into Tims Branch. Increased flow velocity can potentially result in resuspension, remobilization and transport of sediment-deposited tin dioxide further downstream.
- GIS technology was applied for delineation of the stream network and features such as nodes and cross sections used for the computation of unsteady flows in rivers and flow over hydraulic structures. GIS tools were also used for geoprocessing of model-specific data required for model development.

Fig 2. Aerial photo of the SRS A/M area near Outfall A-014

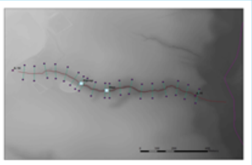


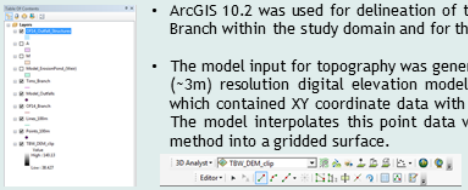
Fig 3. A topographic view of Tims Branch in the area near Outfall A-014

Study Area

- This study focuses on the outfall tributary of Tims Branch near the A-014 outfall of the A/M area at the Savannah River Site (SRS) in South Carolina.
- SRS is in the sand-hills region of South Carolina and covers approximately 800 km^2. It encompasses parts of Aiken, Barnwell and Allendale counties and is bordered on the west by the Savannah River and the state of GA. (Fig 4).

Fig 4. Location of Savannah River Site, SC

Methodology



- ArcGIS 10.2 was used for delineation of the cross-sections along Tims Branch within the study domain and for the topographical input.
- The model input for topography was generated by converting a 10 foot (~3m) resolution digital elevation model (DEM) to a point shapefile which contained XY coordinate data with associated elevation values. The model interpolates this point data via a triangular interpolation method into a gridded surface.

Fig 5. Tools used in ArcGIS to generate the stream network cross-sections

Results

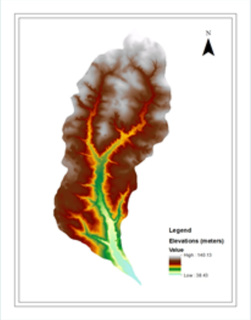


Fig 6. Digital Elevation Model (DEM) of TBW

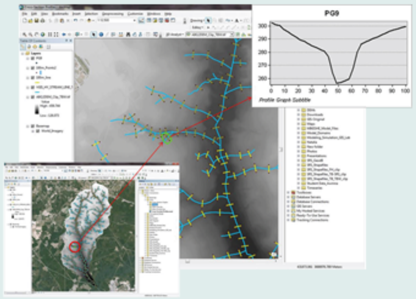


Fig 7. Cross-sections (100m) of TBW

The Role of GIS

- Geographic Information Systems (GIS) enables hydrologists to pre-process and integrate data derived from different coordinate systems, spatial references, scales and time periods, into a single manageable system. ArcGIS provides a suitable platform for conducting geospatial analyses.
- GIS tools are versatile in visually displaying research results via maps, graphs and reports which help enhance the understanding and interpretation of model-derived data and to obtain a perception closer to reality.

Conclusion

- From the cross-sections shown in Fig. 8, changes in the elevation are observed before and after man-made structures that were built, such as the riprap and weir.
- River depth also increases as you go further downstream from A-014, resulting in increased flow rates during high rainfall and possible remobilization of tin dioxide deposited in the sediment.
- Changes in the elevation before and after the cross-section for the riprap is much more significant than the weir.
- This could be because of its slope, creating a higher velocity of water flow and greater erosion.

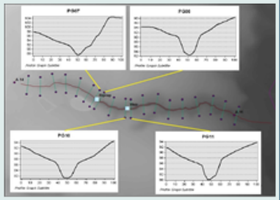


Fig 8. Cross-sections (100m) of structures

Future Work

- To collect topographic information/data over a timeseries of the 1950's, 1980's, and 2000's. This will be used to examine possible impact of the lands topography on Tims Branch Watershed hydrology, and to determine if resuspension and remobilization of tin dioxide has traveled further downstream.
- Cross-sections will be expanded over the entire Tims Branch watershed to be used for a flow simulation in MIKE 11.

Acknowledgements

- Dr. Mehrnoosh Mahmoudi
- Ms. Angelique Lawrence
- Dr. Shimelis Setegn
- Dr. Leonel Lagos
- DOE-FIU Science and Technology Workforce Development Program
- This research was supported by the U.S. Department of Energy, Office of Environmental Management Under Cooperative Agreement # DE-EM0000598

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FLORIDA INTERNATIONAL UNIVERSITY

Using GIS for Processing, Analysis and Visualization of Hydrological Model Data

Angelique Lawrence[1], Mehrnoosh Mahmoudi[1], Shimelis Setegn[1], Natalia Duque[1] (DOE Fellow), Awmna Rana[1] (DOE Fellow), Brian Looney[2]
[1]Applied Research Center - Florida International University, Miami, FL; [2]Savannah River National Laboratory, Aiken, SC

FIU Applied Research Center

BACKGROUND

Water discharged to the Tims Branch stream located at the U.S. Department of Energy's Savannah River Site in Aiken, SC, contains trace levels of inert and nontoxic tin (IV) oxide, which is well below the limits for ecological toxicity. This was derived from the addition of tin (II) chloride to Tims Branch as a remediation technology which successfully reduced legacy mercury contamination in TBW to below regulatory levels.

ISSUE

Outside scientists have postulated the potential for tin methylation and tin mediated mercury methylation during extreme rainfall events where there is the possibility of resuspension, remobilization and transport of tin downstream to areas where environmental conditions are favorable. Additionally, tin solids are subject to accumulation in various compartments in the ecosystem.

ACTION

A hydrological model is being developed by the Applied Research Center at Florida International University to simulate flow and contaminant transport in TBW during extreme rainfall events.

ArcGIS tools are being used for model-specific data preparation and to conduct geospatial analyses using timeseries data to examine features such as land cover/land use change and contaminant concentration before and after implementation of the remedial strategy in Tims Branch.

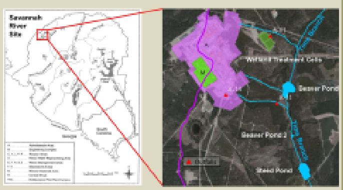


Fig. 1. Point of water discharge from the SRS A/M area into Tims Branch

METHOD

1. Development of an ArcGIS Geodatabase.
2. Pre- and post-processing of hydrological model data using ArcMap and ArcToolbox.
3. Use of ArcGIS ModelBuilder & Python scripting:
   - Automate repetitive geoprocessing tasks.
   - Perform statistical calculations.
   - Generate maps and reports.
4. Use of ArcGIS Geodatabase Diagrammer to create, edit or analyze geodatabase schema.

Development of an ArcGIS Geodatabase

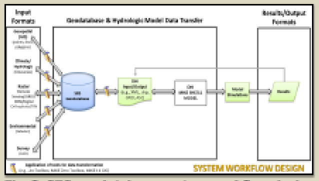


Fig. 2. SRS geodatabase system workflow design

SRS Geodatabase (Fig. 2):

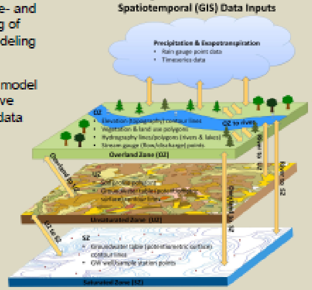
- A multiuser relational database management system deployed on an advanced Windows server using ArcGIS for Server.
- Based on ArcHydro and ArcGIS Base Map data models which had several input data types in common with the SRS Geodatabase.
- ArcHydro has tools to support water resources applications within the ArcGIS environment.
- Modifications made for project specific input parameters.

- Serves as a centralized data management system.
- Provides access to data generated from simulations of contaminant fate and transport to all users.
- Facilitates storage, concurrent editing and import/export of model configuration and output data specific to the hydrologic and transport models being used.
- Structured to be replicable for application at other DOE sites.

Pre- and Post-Processing of Model Data using ArcGIS

- ESRI's ArcGIS software was used for pre- and post- processing of hydrological modeling data.
- The MIKE SHE model uses an extensive amount of GIS data inputs (Fig. 3).

Fig. 3. MIKE SHE Model Spatiotemporal (GIS) Data Inputs



- Development of hydrological models requires data that may include thousands of groundwater monitoring wells, boreholes, stream reaches with gauges, weather stations, land cover, vegetation, soil type, topography, geology, water quality and satellite imagery (Fig. 4).
- GIS enables hydrologists to pre-process and integrate data derived from multiple sources that are usually in different coordinate systems, have different spatial references, are at different scales, and are from different time periods, into a single manageable system.
- GIS can also serve as a useful tool in visually displaying research results via maps, graphs and reports which help to enhance the understanding and interpretation of model-derived data and to obtain a perception closer to reality.

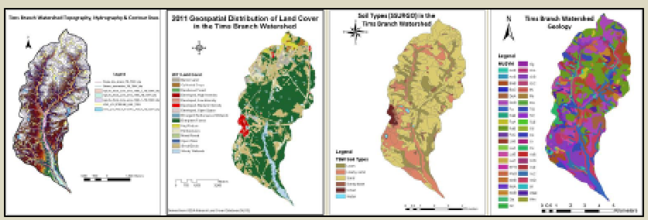


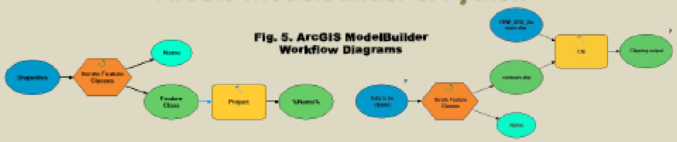
Fig. 4. Gridded input data files used for model development

ACKNOWLEDGEMENTS

This research is sponsored by the U.S. Department of Energy Office of Environmental Management under cooperative agreement # DE-EM0000598.

ArcGIS ModelBuilder & Python

Fig. 5. ArcGIS ModelBuilder Workflow Diagrams



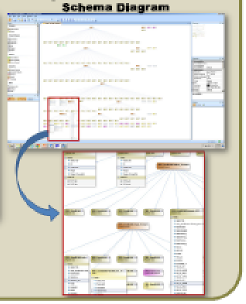
- Python scripts were used to customize built-in ArcGIS tools to automate repetitive model-specific geoprocessing tasks using ArcGIS ModelBuilder such as:
  - Adding GIS files to ArcMap and creating layer files.
  - Selecting features within a specified area (e.g. the study domain) and zooming to selected features.
  - Clipping/extracting selected features and creating a new layer file of selected subset.
  - Exporting clipped features in a format to be used in the MIKE SHE/11 model.
  - Exporting attributes of clipped features in MS Excel or text format for statistical analysis and generation of graphs and reports.
  - Exporting map extents in various formats (e.g. JPEG, TIFF or PDF) for development of reports.
  - Interpolating timeseries data collected at various monitoring points, generating gridded surfaces, and creating and exporting mapped results.
- A toolbox was developed that is scalable and reusable at other DOE sites.
- ArcGIS ModelBuilder generates model workflow diagrams (Fig. 5) to document and visually represent tools and scripts incorporated in the data model.

ArcGIS Geodatabase Diagrammer

- Details of the SRS geodatabase and schema were generated using ArcGIS Geodatabase Diagrammer.
- ArcGIS Diagrammer is essentially a productivity tool used to create, edit or analyze geodatabase schema.
- It generates reports (Fig. 6) and diagrams (Fig. 7) in the form of editable graphics and serves as a visual editor which accepts XML workspace documents that are created from ESRI's ArcMap or ArcCatalog.
- Reports generated depict the geodatabase data structure and details of the features, rasters and tables used during hydrological model development, as well as any existing relationships and spatial references.

Fig. 6. ArcGIS Geodatabase Diagrammer Data Report

Fig. 7. SRS Geodatabase Schema Diagram



BENEFITS & PATH FORWARD

- GIS-based hydrologic models can provide a spatial element that other hydrologic models lack, enabling visualization of model-derived research results via maps, graphs and reports.
- The geodatabase has provided an advanced spatial data structure to assist hydrologists in management, processing, integration and analysis of spatiotemporal numerical modeling data derived from multiple sources.
- GIS can be used to combine different layers of geographic data to create new integrated variables.
- ArcGIS ModelBuilder coupled with Python scripting has enabled the automation of many of the repetitive geoprocessing tasks which facilitated faster and hence more complex analyses of field test data. The toolbox created is a scalable and reusable application that can be implemented at other DOE sites.
- Geoprocessed data will be used for hydrological model development and to conduct geospatial analyses that examine features such as land cover change and precipitation before and after implementation of the remedial strategy employed at Tims Branch to determine if they have any impact on the watershed hydrology.

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Application of Geospatial Tools to Support Development of a Hydrological Model of the Tims Branch Watershed in Aiken, SC

Awmna Rana – Department of Energy Fellow, Florida International University

FIU Applied Research Center

Introduction & Background

- Tims Branch Watershed (TBW) is a riparian system that makes up a portion of the well known and popularly studied ecological research site in North America, the Savannah River Site (SRS).
- Approximately 1.8 billion gallons of radioactive and hazardous waste was disposed at SRS impacting the surface and groundwater of the surrounding watersheds, including TBW. The waste, particularly uranium and heavy-metals, was produced as a result of nuclear weapons material manufacturing in the 1950s cold war era.
- This research focuses on the development of a GIS-based hydrological model to simulate flow and contaminant (mercury and tin) transport in TBW during extreme rainfall events, where there is the possibility of contaminant remobilization and transport downstream.

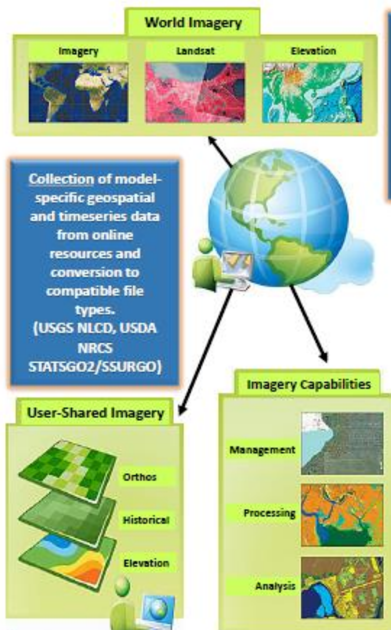
Figure 1. Regional location of the SRS A/M Area, and Tims Branch Watershed

Objectives

- Development of a GIS-based hydrological model to simulate flow and contaminant transport in TBW during extreme rainfall events.
- GIS technology will be used for:
  - Development of an ArcGIS Geodatabase.
  - Hydrological Model Data Processing.
  - Geospatial Timeseries Data Analysis.

Figure 2. Generalized process-based conceptual model of Tims Branch

Methodology & Results



Collection of model-specific geospatial and timeseries data from online resources and conversion to compatible file types. (USGS NLCD, USDA NRCS STATSGO2/SSURGO)

Figure 3. Collection & pre-processing of model input data

ArcGIS tools were used for customization of the properties of individual data layers such as the symbology of attributes, color scheme and pixel resolution (Figures 4a and 4b).

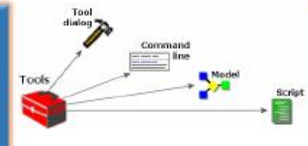


Figure 5. ArcToolbox used for statistical calculations, data customization and visualization

Statistical calculations and generation of thematic maps and graphs for visualization of spatiotemporal changes in model parameters.

Figure 4a.

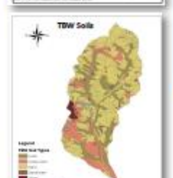


Figure 4b.

Pre-processing of hydrological model data using ArcMap and ArcToolbox. This included:
- **Clipping data to study domain.**
- **Projecting data to relevant coordinate system.**
- **Appending/ formatting relevant attribute data.**
- **Importing associated metadata (XML file).**

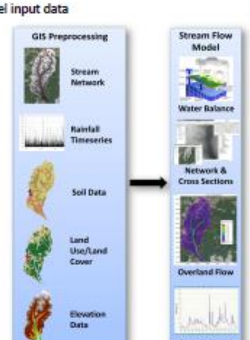


Figure 6. ModelBuilder process flow diagram for clipping data to model domain

ArcGIS ModelBuilder was used for automation of repetitive geoprocessing tasks. ModelBuilder allows individual variables to run through an algorithm in order to analyze, extract, or modify parent data.

Benefits of Using Geospatial Tools

- GIS-based hydrologic models enable visualization of research results via maps, graphs and reports.
- A geodatabase provides an advanced spatial data structure for management, processing, integration and analysis of spatiotemporal data derived from multiple sources.
- Model development is accelerated by use of ArcGIS tools for spatiotemporal data processing.
- GIS tools can be used to combine different geographic data layers to create new integrated variables.
- A customized, scalable geoprocessing toolbox can be created for implementation at other DOE sites.

Future Work

- Geoprocessing and refinement of downloaded data to support hydrological model development.
- Geospatial analysis of timeseries data to examine possible impact of land cover/land use change on Tims Branch watershed hydrology.
- This will involve an integration of GIS and remote sensing technology, the application of statistical methods and the use of hydrological modeling results.

ACKNOWLEDGEMENTS

Mentors:
Angelique Lawrence
Dr. Mehrnoosh Mahmoudi
Dr. Brian Looney
Dr. Leonel Lagos

FIU - Applied Research Center

Savannah River National Lab

DOE-FIU Science & Technology Workforce Development Program

This research was supported by the U.S. Department of Energy's Office Of Environmental Management Under Cooperative Agreement # DE-EM0000598

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Green & Sustainable Remediation Analysis of a Packed Tower Air Stripper Used to Remediate Groundwater Contaminated with CVOCs

Yoel Rotterman, DOE-Fellow

Applied Research Center

Introduction

The Savannah River Site (SRS) located in Aiken, SC, produced materials used in the production of nuclear weapons from the 1950s to the 1980s.

Trichloroethylene (TCE) and tetrachloroethylene (PCE) were the main solvents used in degreasing and other industrial operations. These solvents are categorized as dense non-aqueous phase liquids (DNAPLs), semi-volatile, and hazardous chemical compounds.

A pilot air stripper followed by a full-scale air stripper began operations in 1983 and 1985, respectively, to remediate the contaminated soil and groundwater.

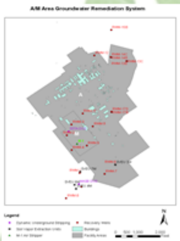

Figure 1. Spatial location of buildings, groundwater wells, soil vapor extraction units, and dynamic underground stripping wells for steam injection in A and M areas.

Problem Statement

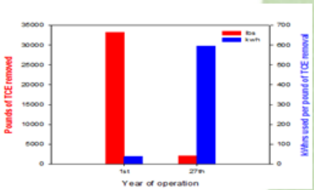

Figure 2. M-1 stripper TCE removal during 1st and 27th years of operation.

The main objective of the air stripper system is the hydraulic containment of the contaminant plume. The air stripper and well network system has operated continuously for over 30 years at an average electrical load of 150 kW and flow rate of 420 gpm, consuming 1.25 million kW-hr of electricity and pumping 2.1 billion gallons per year. The air stripper removed 33,231 pounds of TCE during its first full year of operation and removed 2,092 pounds of TCE during its 27th year of operation while consuming the same amount of electricity and removing the same amount of groundwater annually.

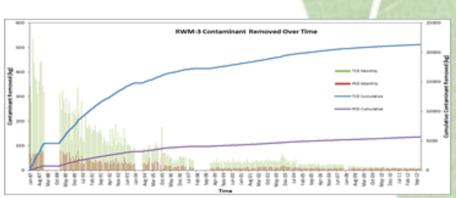

Figure 3. RWM-3 cumulative and monthly TCE and PCE mass removed.

Purpose

Green and Sustainable Remediation (GSR) involves the use of technologies, processes, protocols and other methods to mitigate the risk of contaminants reaching receptors while informing decision making with environmental, economic and community impacts. An optimized remediation system may consume less energy, pump less water, cost less and yet provide equal or greater environmental protection.

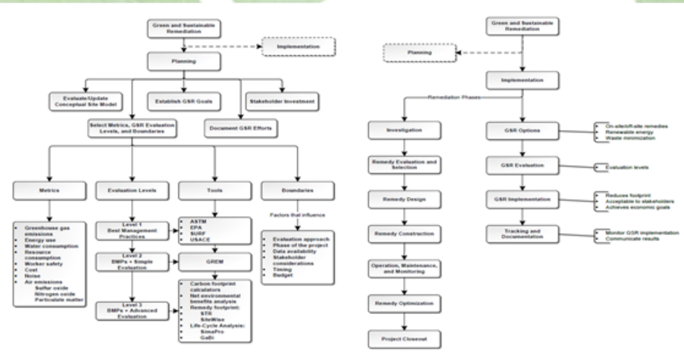

Figure 4. GSR Planning and Implementation Flowchart.

M-1 Air Stripper and Pump System

Since April 1985, contaminated groundwater in the A/M Area on the northern part of SRS has been treated with the M-Area groundwater remediation system (GRS) which consists of: a custom full-scale air stripper, an air blower with variable speed drive, a tails pump, air system instruments, a control building with associated piping instrumentation and controls and submersible groundwater pumps for each recovery well in the network.

The air stripping process is a mass transfer operation that provides contact between air and water, moving the VOCs from the water to the air.

Figure 5. Photograph of the full-scale M1 air stripper at M-Area at SRS.

Recommendations

Solar

- FIU recommends a solar photovoltaic (PV) system be installed to power the air stripper.
- Solar power is clean and sustainable.
- The cost has declined steadily in recent years making solar more cost-effective. The total electrical power generation capacity in the USA has greatly increased in the past decade.
- A solar alternative from Southern Atlantic Solar Company (see Figure 6) for \$2.3M is estimated to pay itself back in 8.65 years under the worst case scenario, that none of the available solar incentive programs would be available

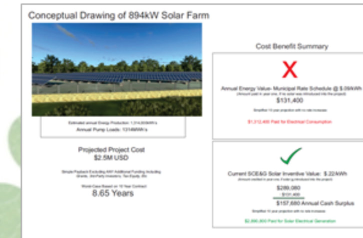

Figure 6. Analysis made by the Southern Atlantic Solar company

Blower

- FIU recommends an analysis be completed for the optimal motor speed sufficient to treat TCE and PCE at the concentrations entering the stripper to the desired 1 ppb release level. This has the potential to save a significant amount of electrical energy.
- The current blower 60 HP, 480V, 3-phase AC motor has a variable speed drive. FIU is not aware if the M1 air stripper blower motor speed has been optimized to a lower speed. A number of documents cite a 2000 cfm value for the blower motor.

Groundwater Modeling

- FIU recommends that a groundwater modeling analysis be completed to optimize the pumping rate for each recovery well and for the entire system that provides hydrologic containment in order to maximize the concentration of contaminants pumped to the stripper with possible lower total groundwater and air flow rates in the stripper.

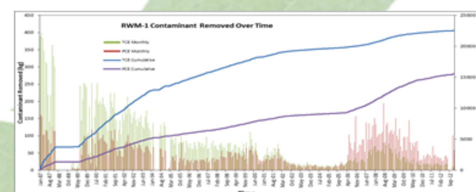

Figure 7. RWM-1 cumulative and monthly TCE and PCE mass removed.

Conclusion

Implementation of the recommendations to optimize the existing remediation system may result in decreasing the energy consumption, volume of water pumped and treated, and overall operating costs, while providing equivalent or improved environmental protection.

Acknowledgements: Dr. David Roelant (FIU-ARC) / Albes Gaona (DOE EM / Natalia Duque (DOE Fellow) / DOE-FIU Science & Technology Workforce Development Program

QUESTIONS

Florida International University