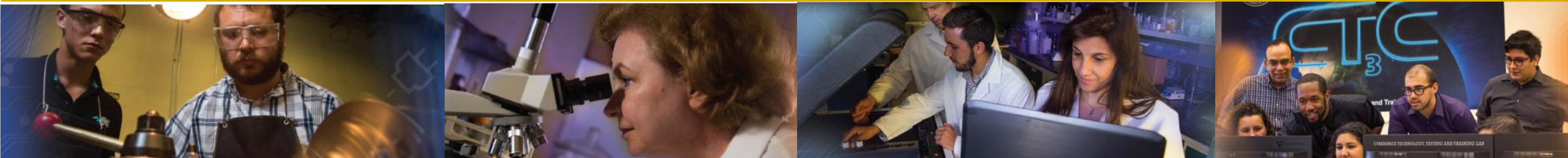
FIU PROJECT 2:
YELENA KATSENOVICH

ENVIRONMENTAL REMEDIATION SCIENCE & TECHNOLOGY

FLORIDA INTERNATIONAL UNIVERSITY



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Project Tasks and Scope

TASK 1: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE HANFORD SITE	
Subtask 1.1	Remediation Research of Ammonia Gas for Uranium Treatment
Subtask 1.2	Contaminant Fate and Transport under Reducing Conditions
Subtask 1.3	Stability of Contaminants in Carbonate Precipitates
Subtask 1.4	Experimental Support of Lysimeter Testing **(NEW)**
TASK 2: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE SAVANNAH RIVER SITE	
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Subtask 2.2	Humic Acid Batch Sorption Experiments with SRS Soil
TASK 3: CONTAMINANT FATE AND TRANSPORT MODELING IN THE TIMS BRANCH WATERSHED	
Subtask.3.1	Modeling of Surface Water Flow and Contaminant Transport in Tims Branch
Subtask 3.2	Application of Geospatial Technologies for Long-Term Environmental Monitoring
Subtask 3.3	Data Collection, Sampling and Analysis in Tims Branch Watershed
TASK 5: RESEARCH AND TECHNICAL SUPPORT FOR WIPP	
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TASK 6: HYDROLOGY MODELING FOR WIPP (NEW)	
Subtask 6.1	Digital Elevation Model and Hydrologic Network
Subtask 6.2	WIPP Hydrologic Database Development
Subtask 6.3	ASCEM GWM and LSM Training

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

Task 1.1 – Remediation Research with Ammonia Gas for Uranium

Site Needs:

DOE-EM has a critical need to understand the geochemical reactions that may occur with pH manipulations via alkaline treatment for uranium sequestration in the vadose zone following release of >200,000 kg of U during WWII and the Cold War. Alkaline pH manipulation is a potential remediation technology that can lead to incorporation of U(VI) into the sediments. These studies will provide information that can potentially aid in the interpretation of long-term monitoring of the disposal sites.

Objectives for FIU FY9:

Identify the physicochemical mechanisms controlling immobilization of U via NH_3(g) injection in the Hanford vadose zone.

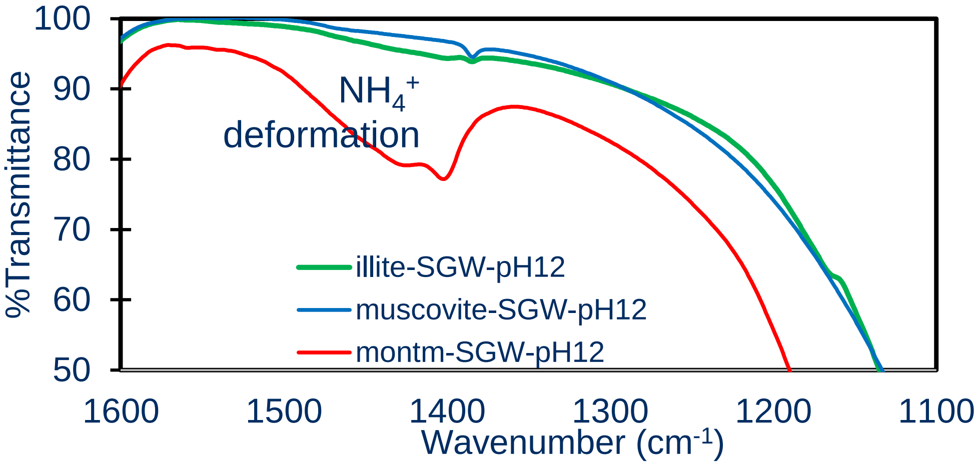
- Measure removal of U from the aqueous phase following NH_3(g) injection.
- Characterize physicochemical changes in minerals.
- Determine the long-term stability of U-solid phases after NH_3(g) injection.

Task 1.1 – Remediation Research with Ammonia Gas for Uranium

FY9 Research Highlights

- Ongoing
  - Characterizing solid phases (with and without U) to identify dominant mineral phases controlling U behavior
  - Long-term (~6 months) aging montmorillonite clay mineral to high U loading for K_d analysis and solid characterization (during treatment pH12 & post treatment pH 8)
- Finalized results measuring mineral dissolution (three-months) of phyllosilicates exposed to aqueous NH_4OH
- FTIR and TEM confirmed montmorillonite's expanding layer
- SEM-EDS shows potential secondary precipitates upon aeration
- SAED on TEM suggests polymorphism and potential amorphous secondary precipitates for montmorillonite.
- EMPA shows Al & Si alignment and strong correlation between U & Fe

5% ammonia/ 95%nitrogen injection for montmorillonite long term U-aging experiment



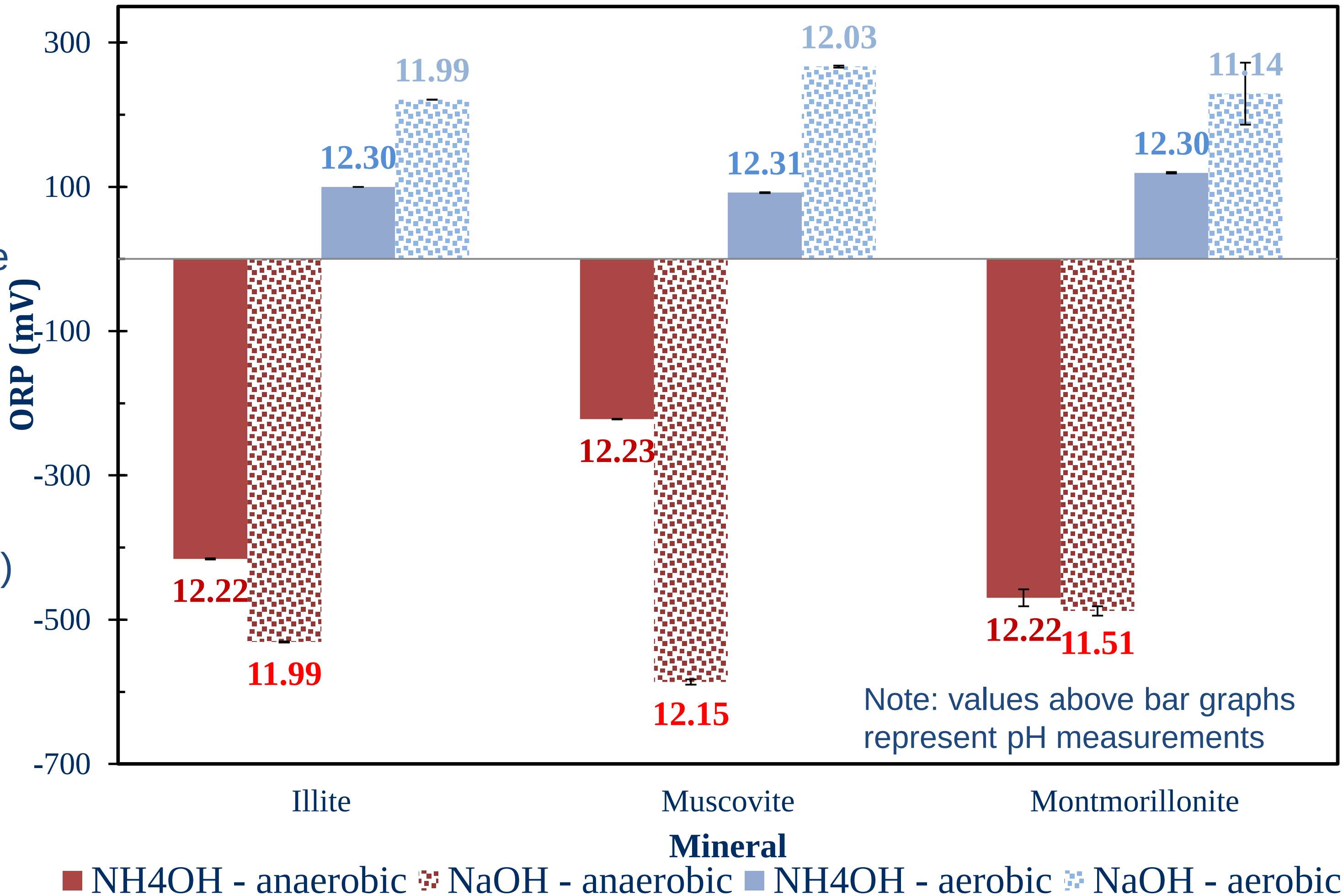
FTIR shows cation (NH_4^+) intercalates montmorillonite but not in illite & muscovite

Task 1.1 – Remediation Research with Ammonia Gas for Uranium

FY9 Research Highlights

- Mineral dissolution expt. background solution measured for redox changes.
- Significant difference in anaerobic vs. aerobic conditions.
- Two theories:
  1. Difference in charged (Na^+ ion) or molecular (NH_3) species?

     OR
  2. Difference in how aqueous species interact with electrode?



Task 1.1 – Remediation Research with Ammonia Gas for Uranium

FY9 Accomplishments

- Publication in *J. Env. Management:* Emerson *et al., "*Potential for U sequestration with select minerals and sediments via base".
- Manuscript in preparation to be submitted to *Applied Clay Science* or *Geochimica and Cosmochimica Acta,* "Phyllosilicate Mineral Dissolution following Alkaline Treatment"
- Awards
  - –*Young Researcher Speaker Award* – SoFL-ACS Chemical Sciences Symposium
  - –*Student Best Poster, 3rd place* – DOE Fellows Poster Competition
- Presentations at Waste Management Symposia (March 2019), Larkin University in Miami (April 2019) and upcoming oral presentation at ACS Meeting in San Diego (August 2019).

Task 1.1 – Remediation Research with Ammonia Gas for Uranium

FY10 Objectives

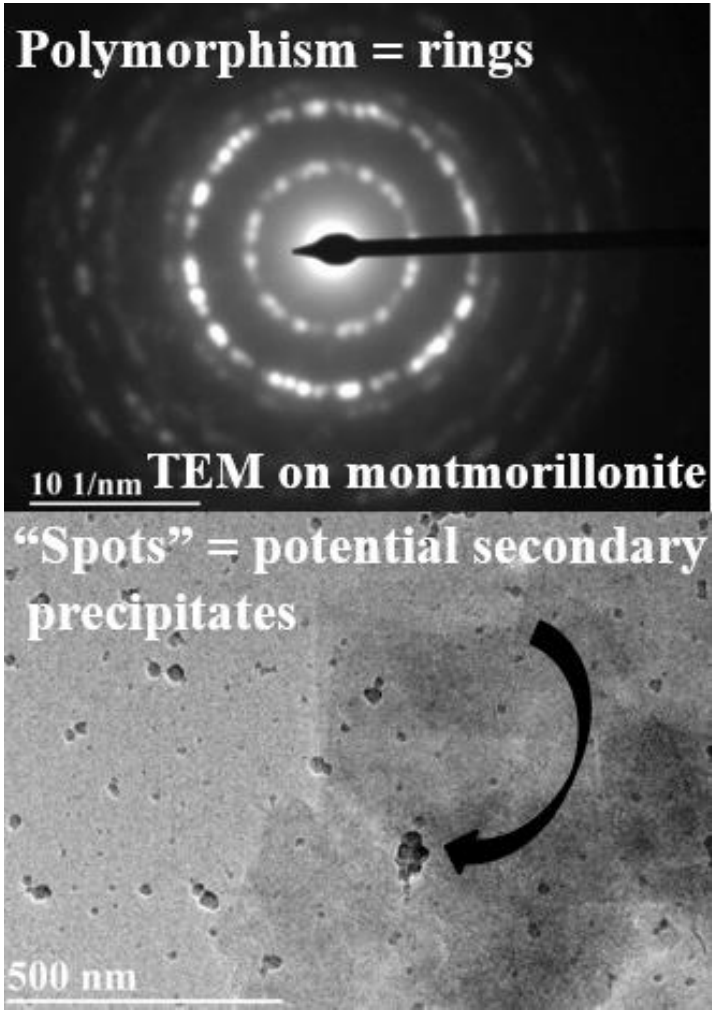
Proposed Scope for Performance Year 10

To understand impacts of base treatment on long-term fate of U:

- Physical and mineralogical changes due to dissolution and precipitation of muscovite, illite, and Hanford sediments
- Speciation of U in the solid phase due to sorption and co-precipitation
- Stability of solid U phases

To be accomplished via:

- TEM, SEM-EDS, EMPA, XRD, and ^{27}Al and ^{29}Si solid-state NMR - conventional characterization techniques to identify secondary mineral precipitates
- Predictive Geochemist WorkBench® Speciation modeling



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

Task 1.2 - Contaminant Fate and Transport under Reducing Conditions

Site Needs:

DOE-EM has a critical need to address challenges associated with Tc-99 remediation of the contaminant plumes in deep vadose zones (*Technetium Management Program Plan (DOE EM, 2016)*). It requires understanding of the fate of Tc in conditions related to the Hanford Site and exploration of the effect of bicarbonates on redox transformations of Tc-99 to facilitate identification of promising Tc-99 remediation technologies.

Objectives for FIU FY9:

Investigate the behavior of Tc in the presence of ferrous iron minerals and bicarbonates.

- Characterize site-specific ferrous iron materials for morphology, particle size and surface area.
- Study the reduction of Tc-99 in the presence of pure minerals such as ilmenite and biotite.
- Monitor ferrous iron concentrations released into the aqueous phase.
- Determine the potential for re-oxidation of prior immobilized Tc(IV) in the presence of ferrous-iron-containing minerals in a media with and without bicarbonate.

Task 1.2 - Contaminant Fate and Transport under Reducing Conditions

FY9 Research Highlights

- Obtained two biotite minerals from Eisco Labs and Carolina Biological Supply
  - Biotite minerals have sheet-like structure.
  - Broken down in agate mortar & pestle and blender to get fine particles.

- Obtained two ilmenite minerals from Ward Scientific
  - Broken down by hammer and agate mortar & pestle to get fine particles.

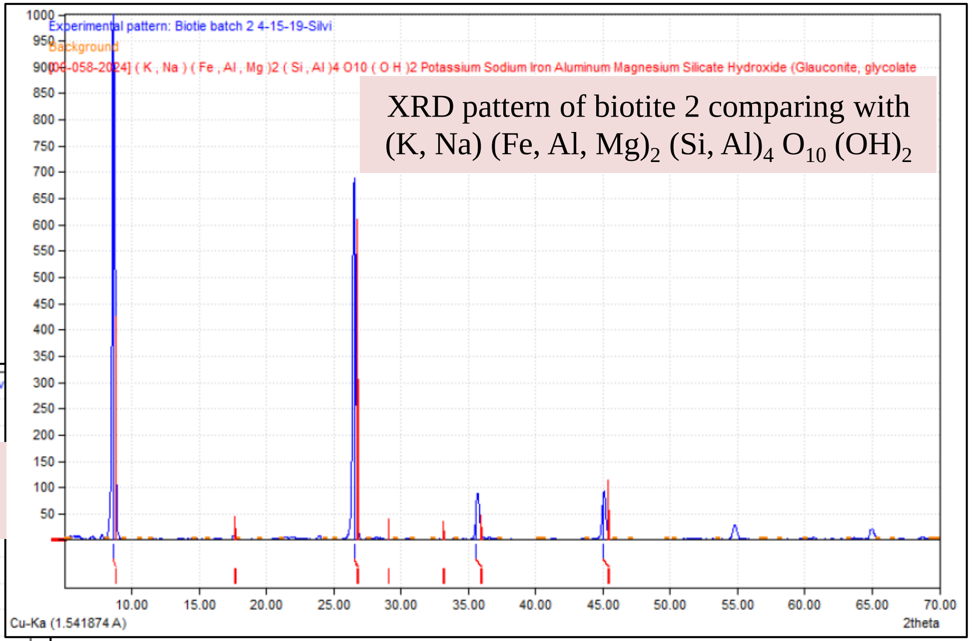
- Samples were sieved through a 300 µm size mesh to ensure an uniform particle size.

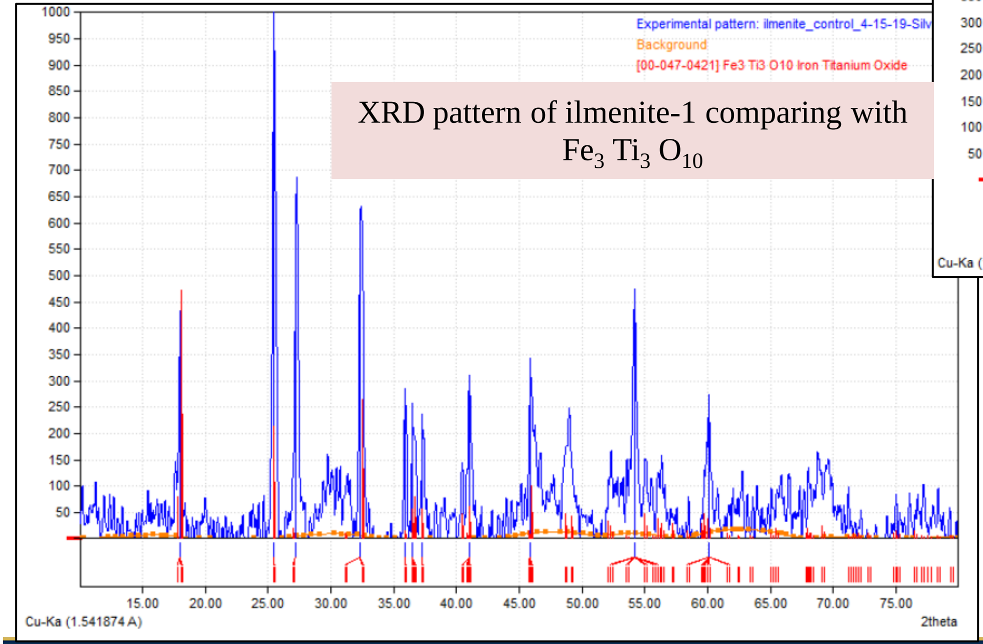
- Performed surface area analysis using BET method, mineralogical analysis via X-ray diffraction (XRD) and surface morphology and elemental composition via SEM-EDS.

Task 1.2 - Contaminant Fate and Transport under Reducing Conditions

FY9 Research Highlights

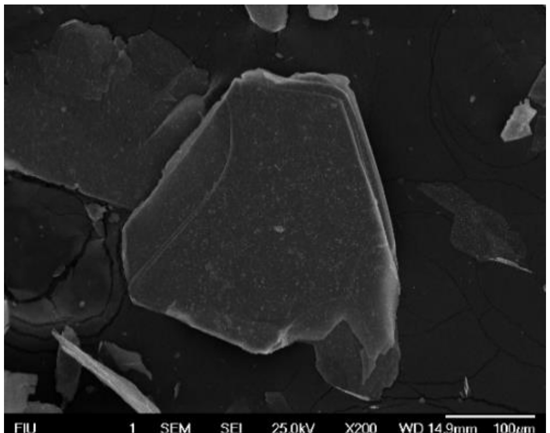
Mineral	BET Surface Area (m2/g)	Pore Volume (cm3/g)	Pore Size (A)
Biotite 1	1.4286	0.005826	163.1253
Biotite 2	1.9227	0.007035	146.3603
Ilmenite 1	0.6154	0.002003	130.1658
Ilmenite 2	0.1204	0.000604	200.6978

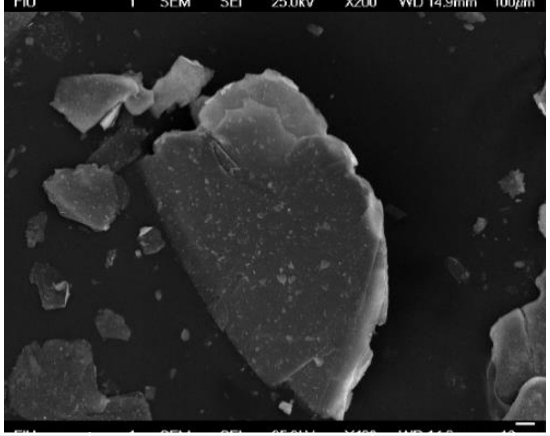


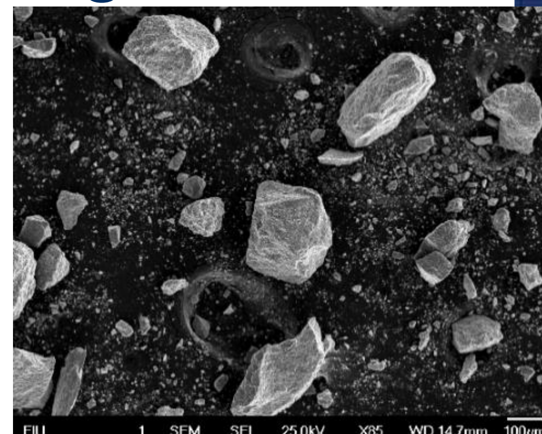


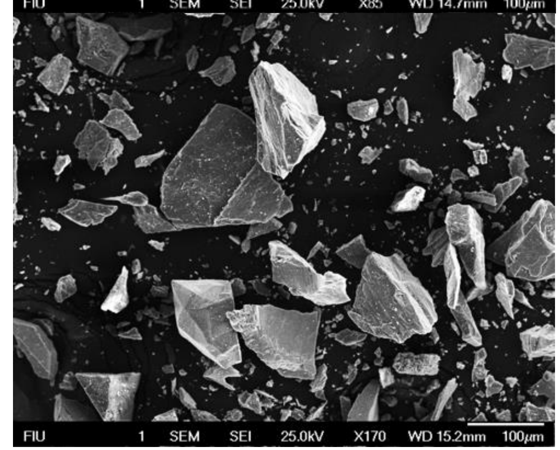
Task 1.2 - Contaminant Fate and Transport under Reducing Conditions

FY9 Research Highlights









	O	Mg	Al	Si	K	Fe
Biotite 1	28.04	8.20	6.44	23.08	10.54	20.37
Biotite 2	24.39	8.88	4.32	21.40	11.33	14.48

	O	Ti	Fe
Ilmenite 1	32.63	41.86	19.57
Ilmenite 2	18.29	24.57	54.23

Task 1.2 - Contaminant Fate and Transport under Reducing Conditions

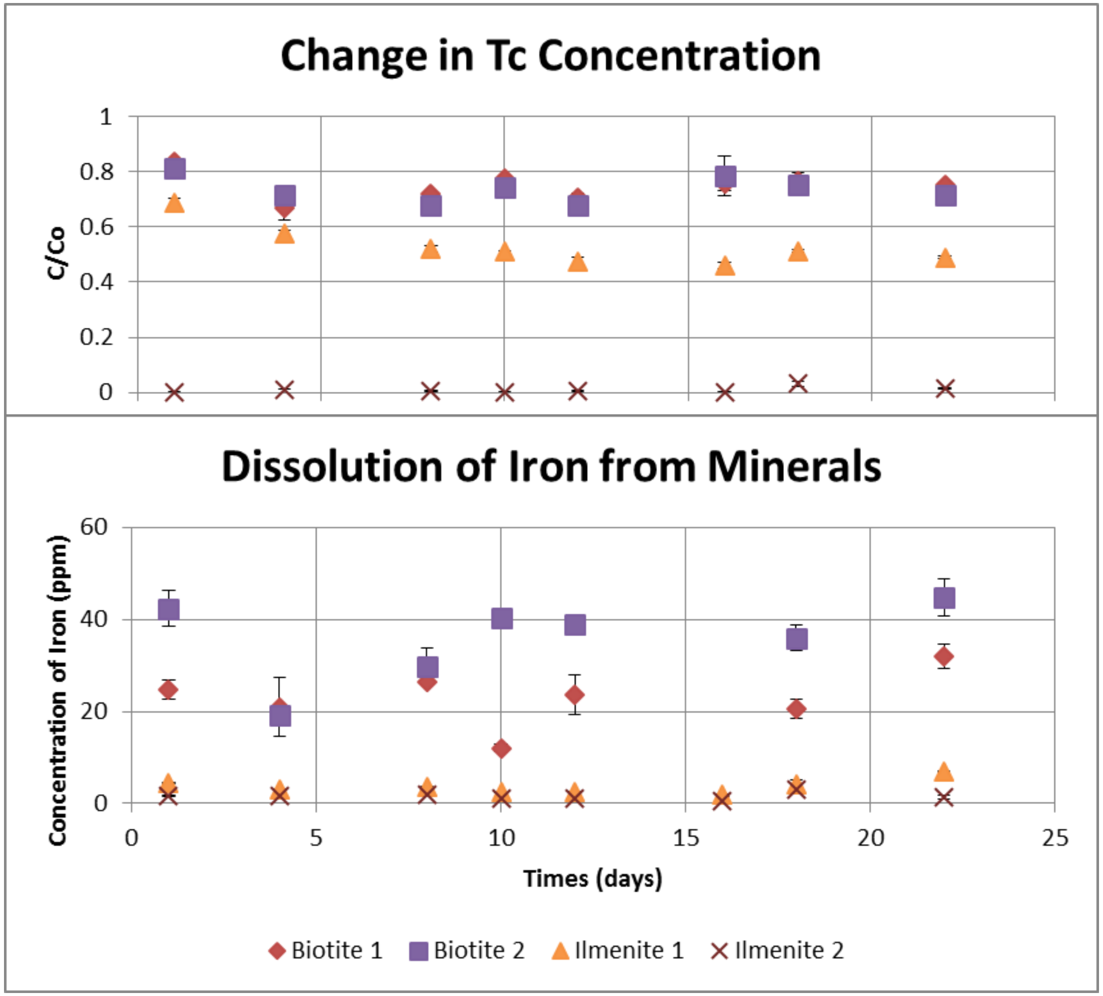
FY9 Research Highlights

Experimental Conditions

- 300 mg of iron minerals
- pH 8
- 1 ppm Tc
- 30 ml sample
- pH adjusted regularly

Results

- 20-30% Tc reduction biotite minerals
- Ilmenite-1 reduced 50% of Tc
- Ilmenite-2 reduced Tc ~100% within one day



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

Task 1.2 - Contaminant Fate and Transport under Reducing Conditions

Ongoing experiments

- Study pertechnetate reduction in the presence of HCO_3^- at pH 8 to compare reduction rates by Hanford sediment and magnetite
- Conduct characterization of magnetite-ferric oxide samples to identify factors responsible for mineral transformation and faster pertechnetate reduction by means of FTIR, XRD and possibly XPS

Objectives for FY10

- Investigate bicarbonate sorption on the surface of ferrous iron minerals at pH 8.
- Investigate re-oxidation rates of reduced Tc in the presence of ferrous-iron-containing minerals with and without bicarbonate

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

Task 1.3 - Stability of Contaminants in Carbonate Precipitates

Site Needs:

Historical ^{129}I releases have resulted in massive, dilute plumes spreading to >50km^2 in Central Plateau subsurface of Hanford Site. Currently, DOE has no approved treatment technologies for subsurface ^{129}I plumes. Previous studies confirmed that iodine can be incorporated into the structure of calcium carbonate, which is a common mineral in the Hanford subsurface. This incorporation is assumed to be mainly as the IO_3^- group substituting for CO_3^{2-}.

Objectives for FIU FY9:

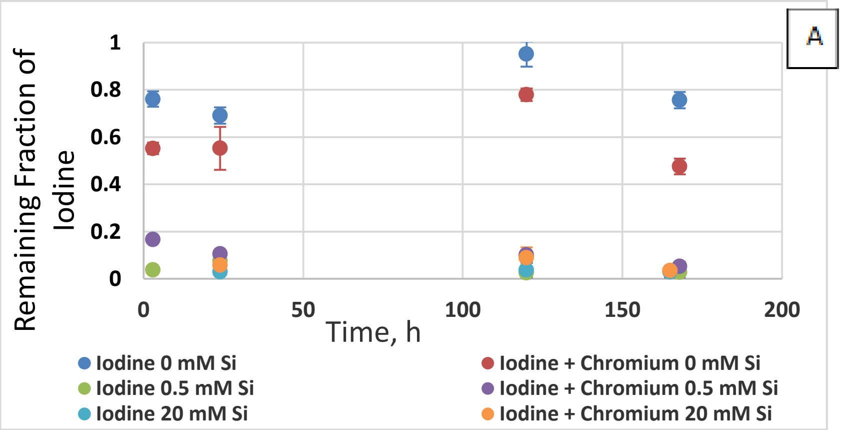
Investigate effect of VZ conditions (pH and silica content) on the iodine co-precipitation process with calcium carbonate in the presence of comingled chromate contamination.

- Study effect of pH (6.5, 8, 9) and silica concentrations (0mM, 0.5mM, 20mM) in 0.1M calcium carbonate forming solutions ($CaCl_2$ and Na_2CO_3) on iodate co-precipitation with calcium carbonate (Iodate is predominant aqueous species of iodine in GW samples at 200-UP-1).
- Conduct iodine and chromium "late spike" experiments after $CaCO_3$ precipitation at different pH and Si concentrations.
- Conduct characterization of solid phases.

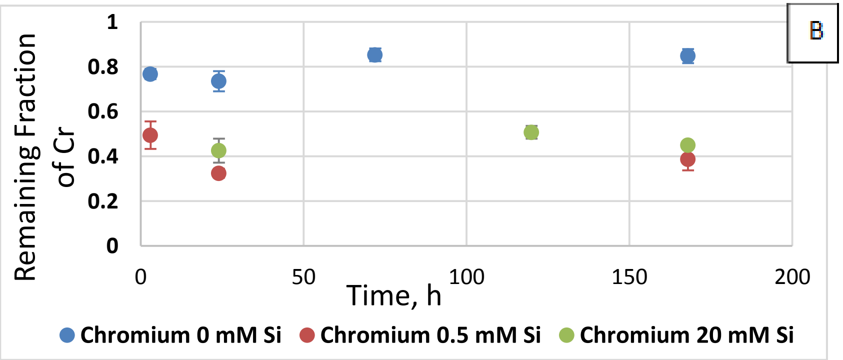
Task 1.3 - Remediation Research on Iodine Incorporation into Calcite

FY9 Research Highlights

- Finalized experiments on iodine incorporation in calcium carbonate in the presence of comingled chromium
  - Iodine and iodine comingled with chromium showed similar percentage of iodine removal.
  - Increase in Si concentrations resulted in higher iodine removal in iodine only and I+ Cr samples
  - Increase in pH reduced iodine removal from both Si-free and Si-bearing samples
  - Removal of Cr is less compared to Iodine.
  - Presence of Si increased Cr removal.
  - No significant difference for the removal of Si between samples prepared with iodine or iodine comingled with Cr.



Removal of iodine from samples with I only and I+Cr at pH 8

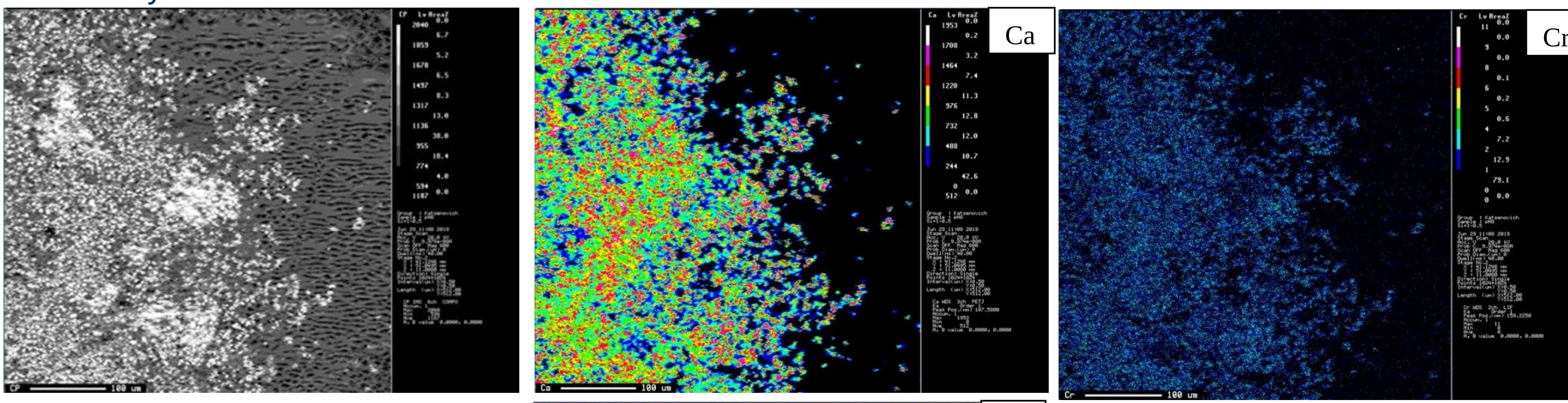


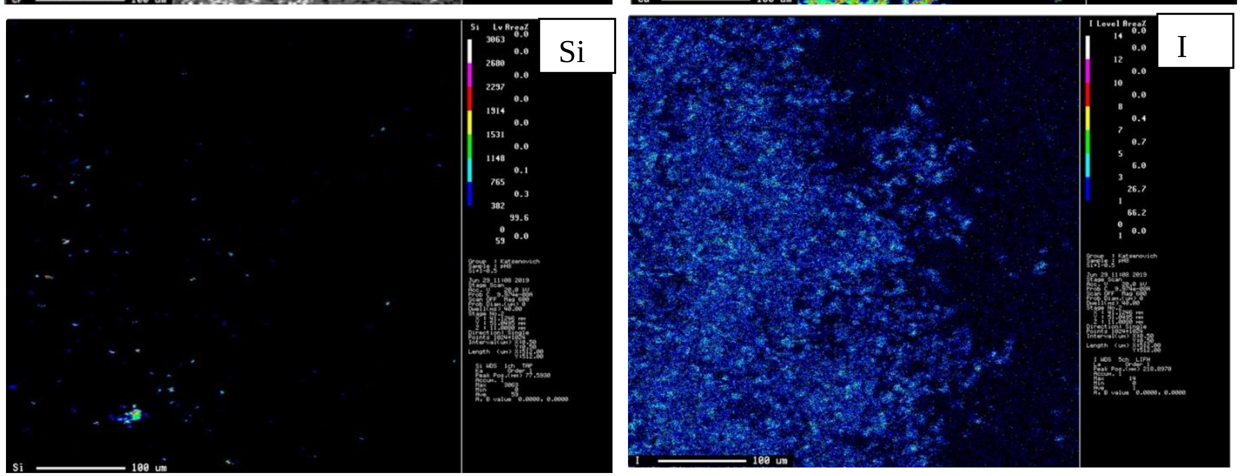
Removal of Cr from samples prepared with I+Cr at pH 8

Task 1.3 - Remediation Research on Iodine Incorporation into Calcite

FY9 Research Highlights

EPMA analysis.





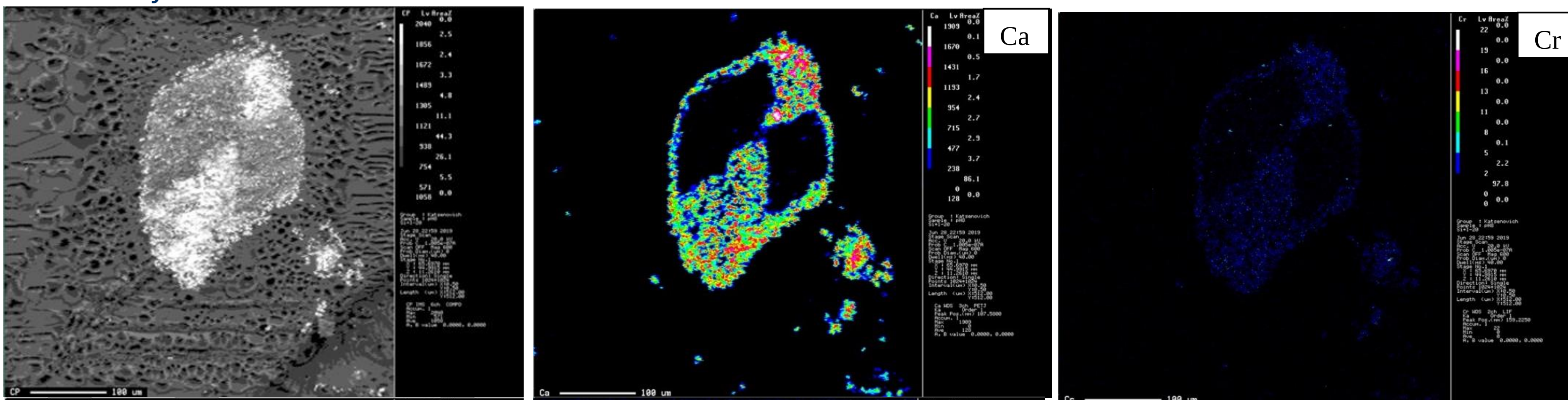
Elemental maps for a sample containing I+Cr at pH 8 and 0.5mM Si

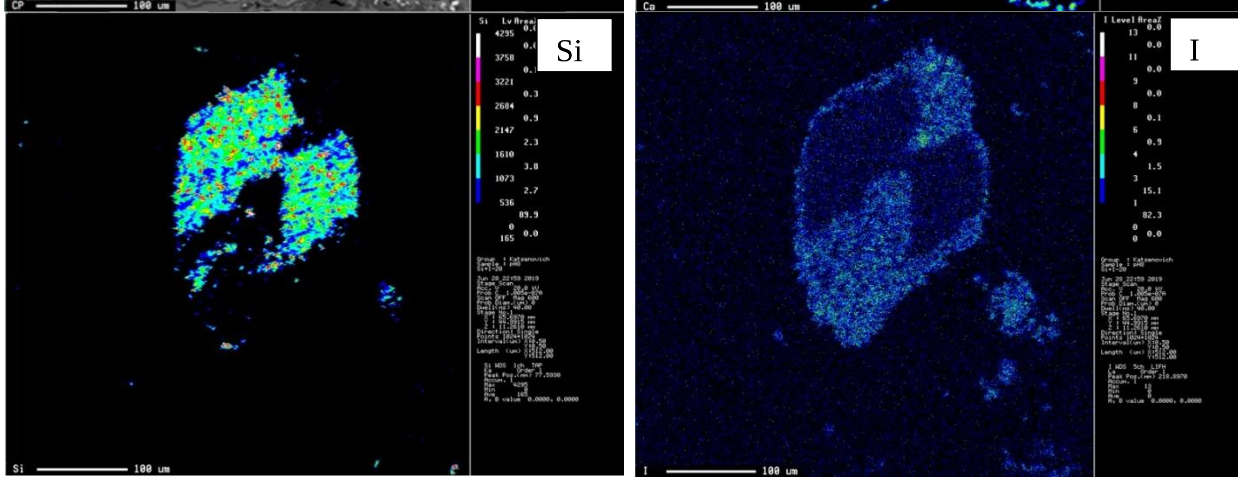
Good alignment of I and Cr with Ca suggesting that iodine and Cr are likely associated with calcite.

Task 1.3 - Remediation Research on Iodine Incorporation into Calcite

FY9 Research Highlights

EPMA analysis.



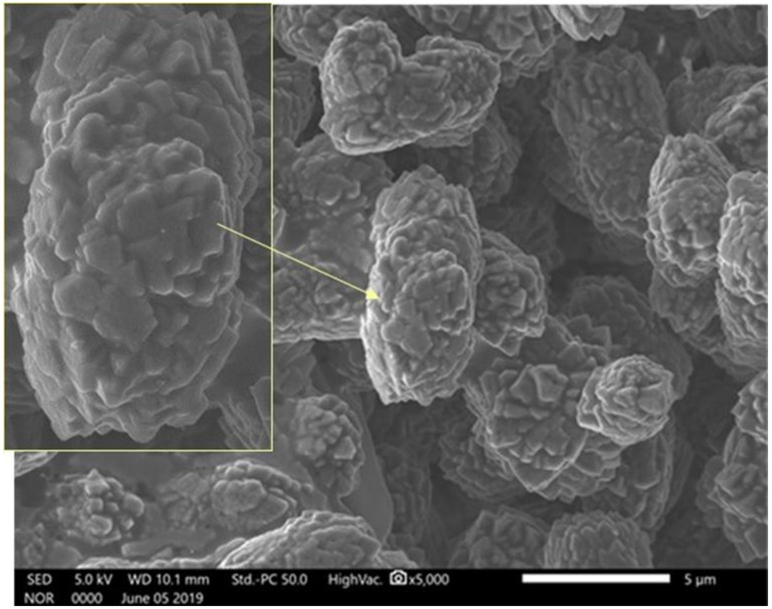


Elemental maps for a sample containing I+Cr at pH 8 and 20mM Si

Iodine shows good alignment with calcium. This suggests iodine association or incorporation into calcium carbonate ppt.

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

Task 1.3 - Stability of Contaminants in Carbonate Precipitates



- Iodine weight %- 2.68±0.29
- Cr weight %- 0.24±0.06
- Cr accumulation in solids is less than iodine; it correlates with less Cr removal from the solution mixture compared to iodine

FY 9 Accomplishments:

2019 Waste Management Conference student poster “Iodine co-precipitation with calcium carbonate”.

Ongoing:

- XRD analysis of solids and complete “late spike” experiments for I and I+Cr samples.
- Iodine &Cr solubility experiments with collected solids
- This task will be completed in FIU year 9.

Year 10 - Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments (NEW)

- Objective - Determine the mechanisms affecting the behavior and fate of contaminants and provide the technical basis needed to assess the long-term effectiveness of MNA at Hanford, thereby supporting Hanford site cleanup.
  - In Year 10 FIU will obtain Hanford sediments and separate size-fractions with significant Fe and Mn phases.
  - Size-fractions and whole sediment samples will be used in a competitive sorption laboratory batch experiments with key contaminants of concern, U, Tc-99, iodine, Cr, and NO_3^-, at the maximum concentrations found in 200A Hanford groundwater and sediments.

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

Task 1.4 – Experimental Support of Lysimeter Testing (New)

Site Needs:

This work supports the disposal of immobilized low-level waste at the Integrated Disposal Facility (IDF) at the Hanford Site. The near-surface location will allow for eventual contact between the immobilized wasteforms (e.g. glass, grout) and groundwater. Long-term field-scale lysimeter testing coupled with laboratory experiments will assist with validating modeling efforts to predict contaminant mobility in the near-field environment present at the IDF. Single-pass flow-through laboratory experiments have been initiated to investigate the effects of grout-contacted groundwater on glass dissolution behavior in support of a recently initiated long-term field-scale lysimeter test.

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

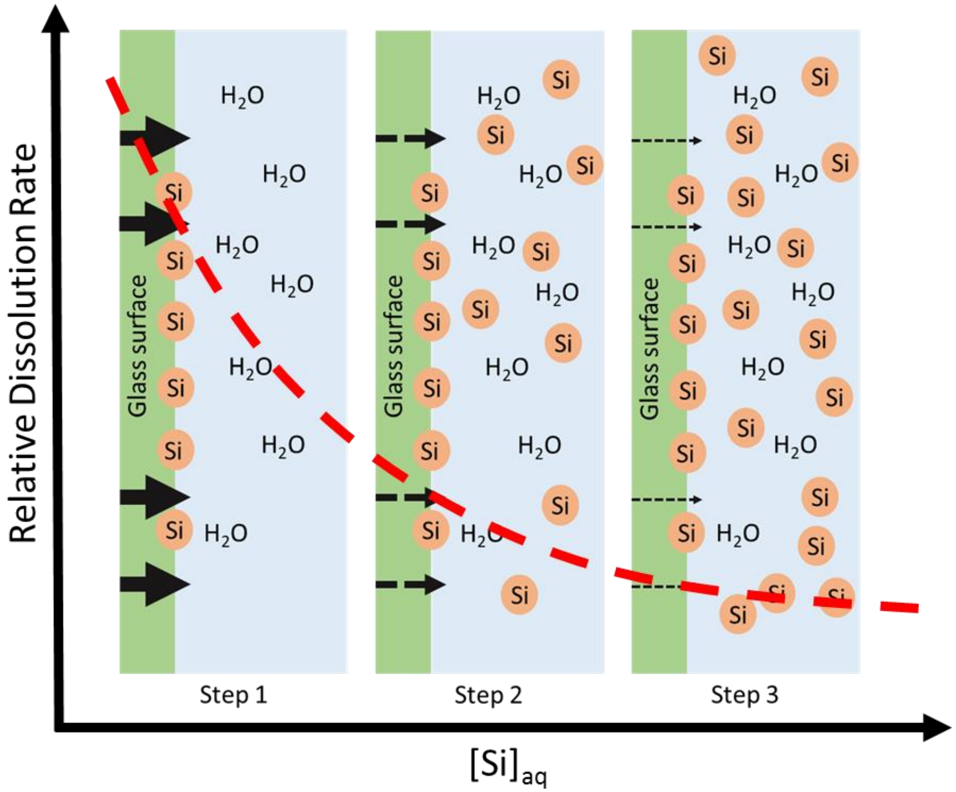
Task 1.4 – Experimental Support of Lysimeter Testing (New)

FIU Applied Research Center

FY 9 Objectives:

To investigate the effect of grout-contacted groundwater on glass dissolution behavior at varying pH (9-12) and temperature (25°C, 40°C, 70°C) using single-pass flow-through (SPFT) and static experiments.

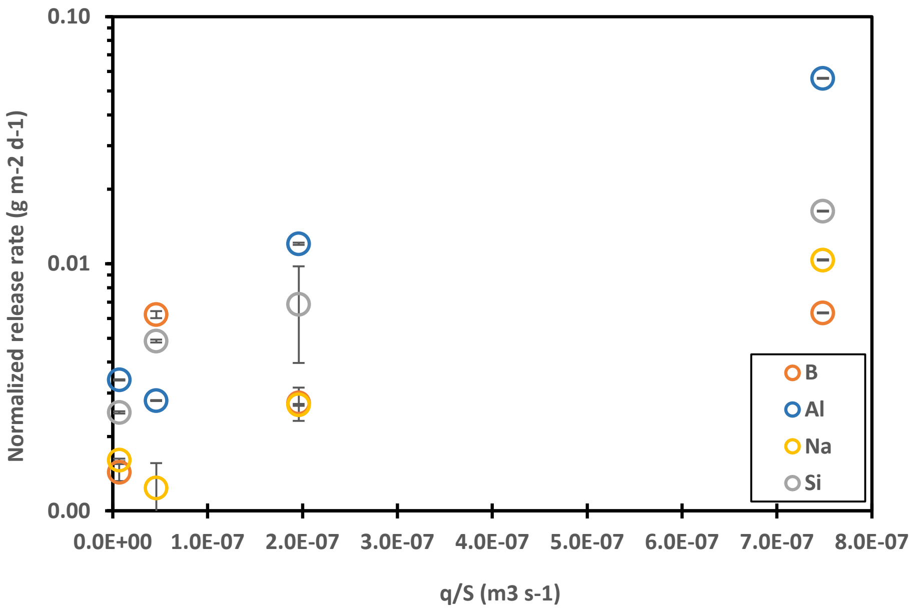
- Determine experimental conditions necessary for forward rate of dissolution.
- Determine baseline glass dissolution behavior.
- Investigate the effect of grout-contacted groundwater on dissolution behavior.
- Investigate possible buffering of glass dissolution in sediment-contacted grout solutions.



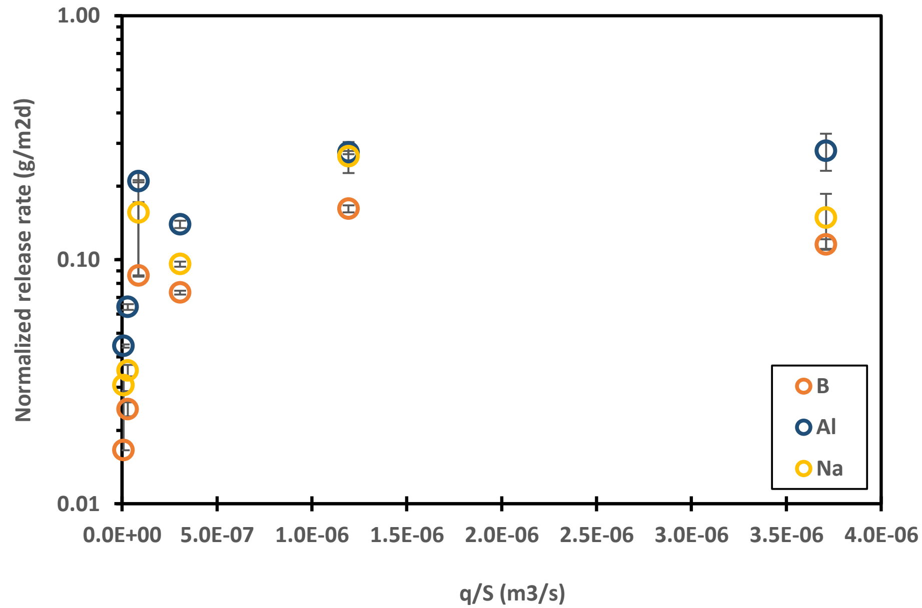
Task 1.4 – Experimental Support of Lysimeter Testing (New)

FY 9 Research Highlights

Release rate of B, Al, Na, and Si at pH 9 and T=25°C



Release rate of B, Al, and Si at pH 9 and T=70°C



Completed q/S sweep to determine conditions necessary for forward rate of dissolution at 25°C and 70°C

Task 1.4 – Experimental Support of Lysimeter Testing (New)

FY 9 Research Highlights

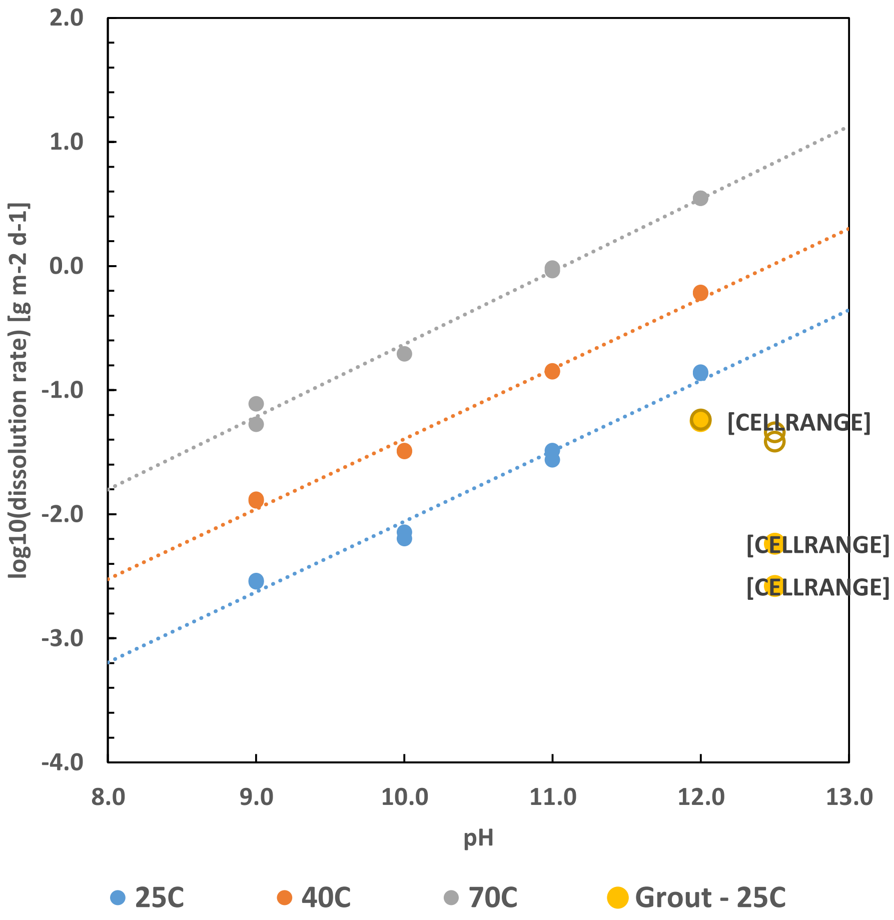
Initiated SPFT experiments utilizing grout-contacted groundwater as the leachate

(Right): B dissolution rates from PNNL-27098 (**Blue**, **Orange**, **Gray**) and B dissolution rates from FIU experiments at 25°C with grout-contacted groundwater (**Yellow**)

Baseline behavior does not appear to predict the behavior observed when grout is present, but further experimentation will give better insight.

Ongoing:

- Results from grout experiments at 40°C are being analyzed
- Grout experiments at 70°C will be completed in August



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

Task 1.4 – Experimental Support of Lysimeter Testing (New)

FIU Applied Research Center

FY 9 Accomplishments:

- Draft of literature review of glass dissolution completed (Milestone 2019-P2-M4)
- Presentation at Fall ACS Meeting on grout-contacted groundwater experiments (August 2019)

FY 10 Objectives:

- Continue evaluating effect of grout on glass dissolution behavior
- Determine if contacting the grout solution with sediment leads to a buffering of dissolution behavior
- Evaluate baseline glass dissolution behavior

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

Task 2.1 - Impact of free radicals on the fate of Tc, I, and U in wetlands at Savannah River Site

Site Needs:

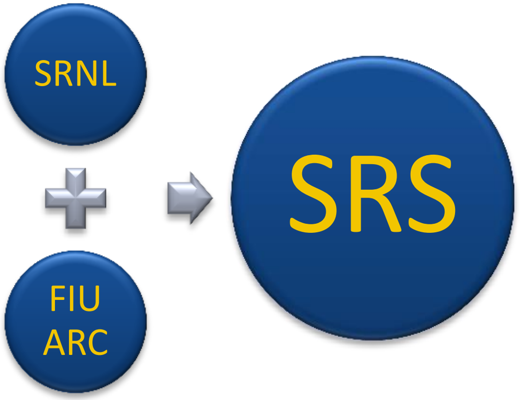
DOE-EM is interested in quantifying the effect of co-mingled contaminant plumes (McCabe et al 2017). This research will supplement ongoing activities at SRS pertaining to the Area Completion Project and associated permitting strategies to evaluate and meet standards for contaminants in the Four Mile Branch Wetland. It will also impact conceptual model development for Tim's Branch Wetland.

Objective in FIU FY9:

To understand I, Tc, and U interactions with reactive oxygen species (ROS) and NOM impacted by ROS due to nitrate and UV interactions

Research Questions:

1. *How do ROS impact organic matter in the presence of nitrate?*
2. *Do ROS or altered organic matter impact the fate of I, Tc, and U?*
3. *Is there a synergetic effect between ROS and organic matter degradation on radionuclide fate?*



FIU Applied Research Center

Task 2.1 - Impact of free radicals on the fate of Tc, I, and U in wetlands at Savannah River Site

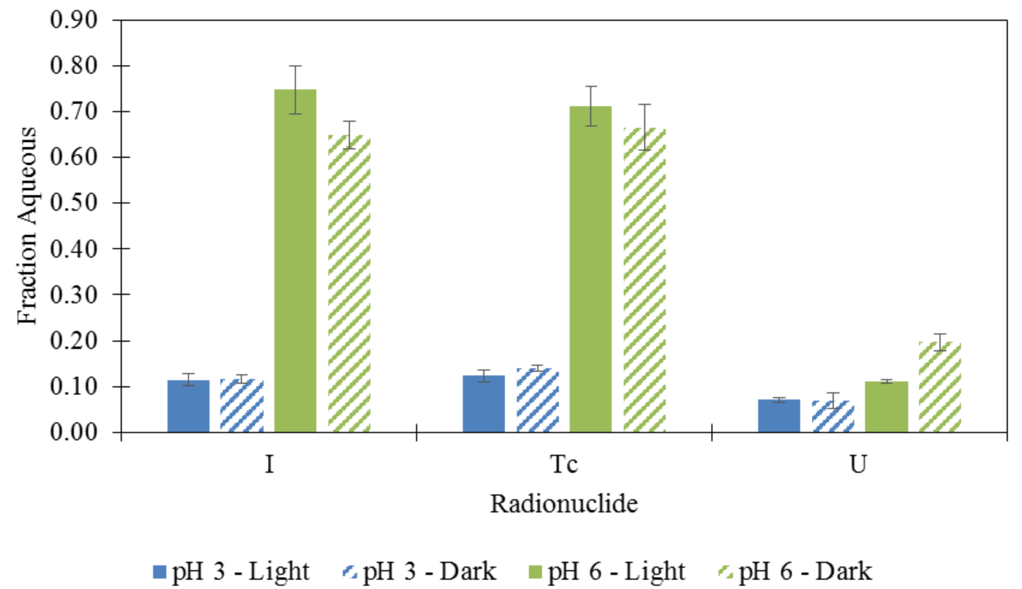
Methodology

- Variable pH (3 - 7) and ionic strength (as $NaNO_3$, 0 to 135 mM)
- Presence or absence of light (via UV lightbulbs)
- Addition of the contaminants before or after light exposure (~100 ppb)
- Sterile or unsterile (via autoclaving): impact that microbes
- Uranium-238, Technetium-99, and iodine-127 analyzed via Inductively coupled plasma mass spectrometer (ICP-MS)
- Natural organic matter analyzed via UV-Vis

Task 2.1 - Impact of free radicals on the fate of Tc, I, and U in wetlands at Savannah River Site

FY9 Accomplishments

- Conducted experiments with Autoclaved SRS sediment
  - 1 g/L peat
  - 135 mM $NaNO_3$
  - 100 ppb Tc, U, I
  - 8 ml sample
  - pH 3, 6



Comparison of E2/E3 Ratios Suggesting Degradation of NOM After 24 hours @ pH 6, significant difference in the total and dissolved fractions in light versus dark

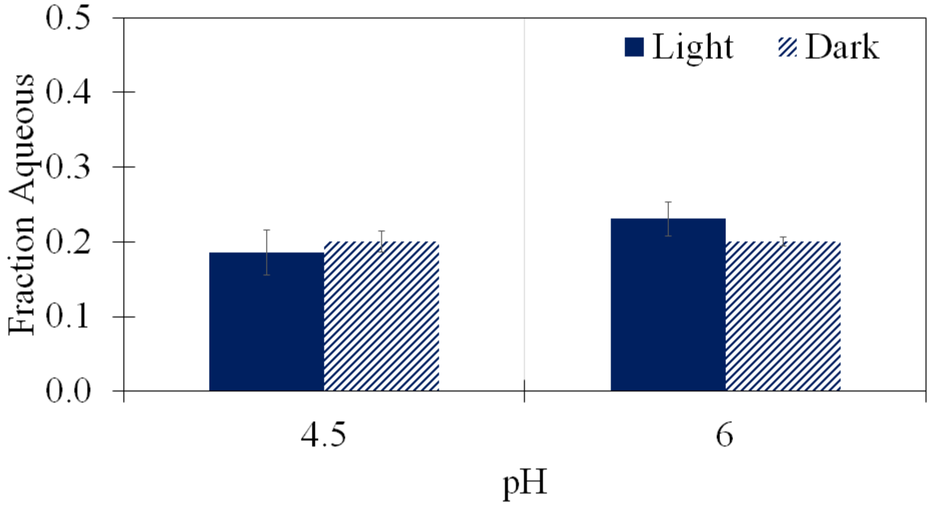
Exposure	Total NOM	Dissolved NOM
Dark	5.8±0.8	5.8±1.9
Light	3.6±0.3	3.2±0.8

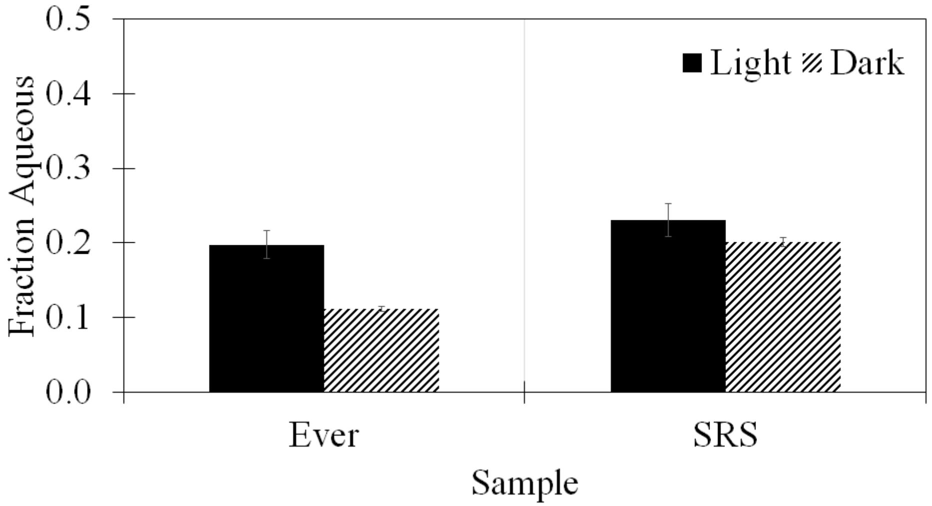
- Similar removal of Tc and I from the aqueous phase occurred under light and dark conditions
- Significant difference for aqueous U with light versus dark treatment (27±3 and 15.1±0.4 μg/L)

Task 2.1 - Impact of free radicals on the fate of Tc, I, and U in wetlands at Savannah River Site

FY9 Accomplishments

- Significant removal of U occurs in the presence of both Everglades and SRS sediments (~ 20% remaining in solution)
- Slightly greater removal of U occurs at pH 6 as compared to pH 4.5
- Slightly greater removal of U occurs in Everglades peat as compared to SRS sediments

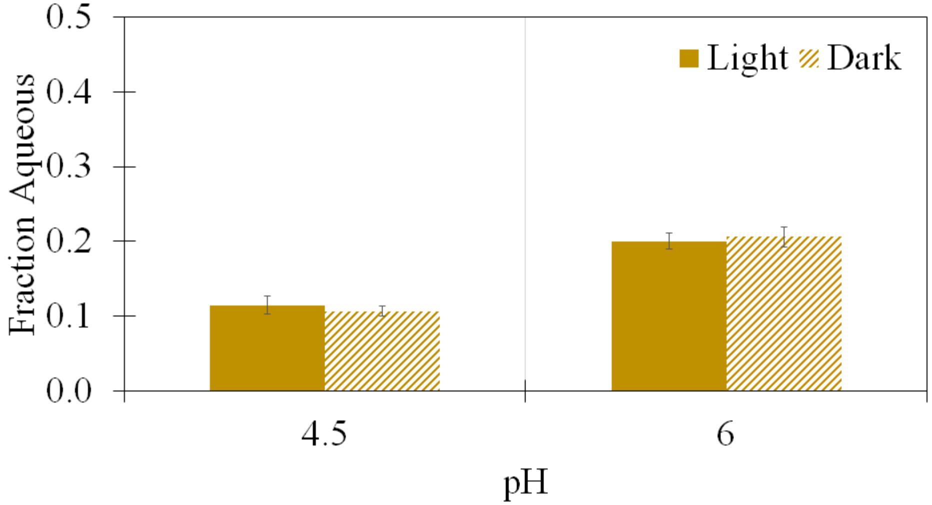


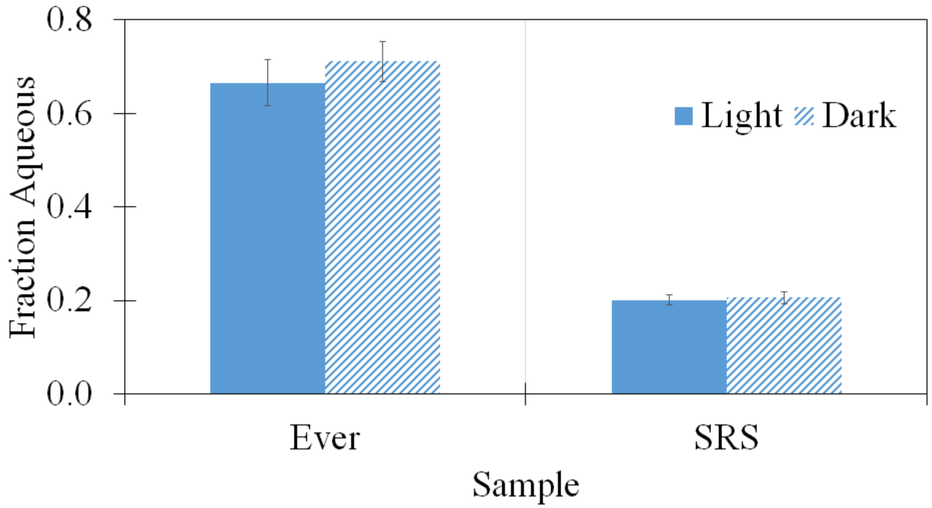


Task 2.1 - Impact of free radicals on the fate of Tc, I, and U in wetlands at Savannah River Site

FY9 Accomplishments

- More Tc-99 is removed at pH 4.5 than pH 6
- Significantly more Tc-99 is removed by SRS sediments compared to Everglades peat



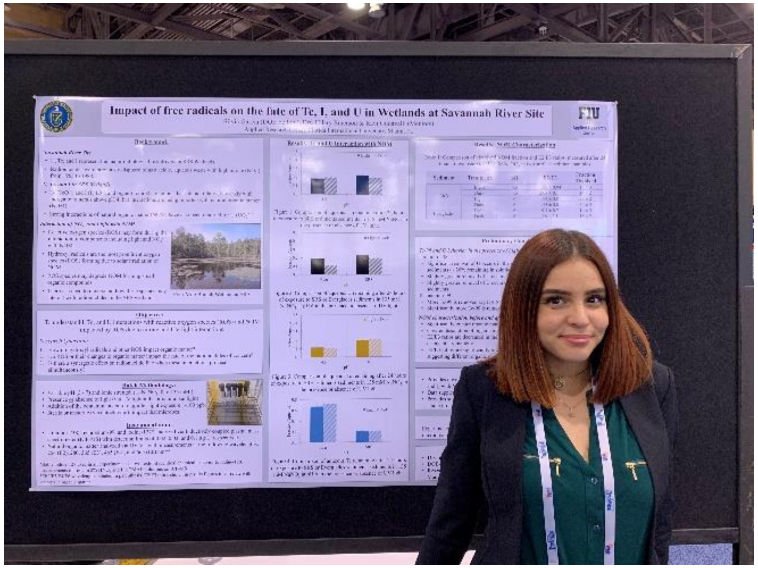


Task 2.1 - Impact of free radicals on the fate of Tc, I, and U in wetlands at Savannah River Site

FY9 Accomplishments & Future Work

- **Accomplishments for FIU Year 9:**
  - Silvia Garcia presented a student poster at WM 2019, LSSF.

- **Ongoing:**
  - Characterization of humic acid via UV-vis, TOC, ATR-FTIR, FT-ICR-MS, and NMR.
  - This task will be completed in FIU Year 9.



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

Task 2.2 - Humic acid batch sorption with SRS soil

Site Needs:

Low cost unrefined humic substances are potential amendments for treatment of uranium in groundwater associated with F-Area Seepage Basins plume.

Objectives:

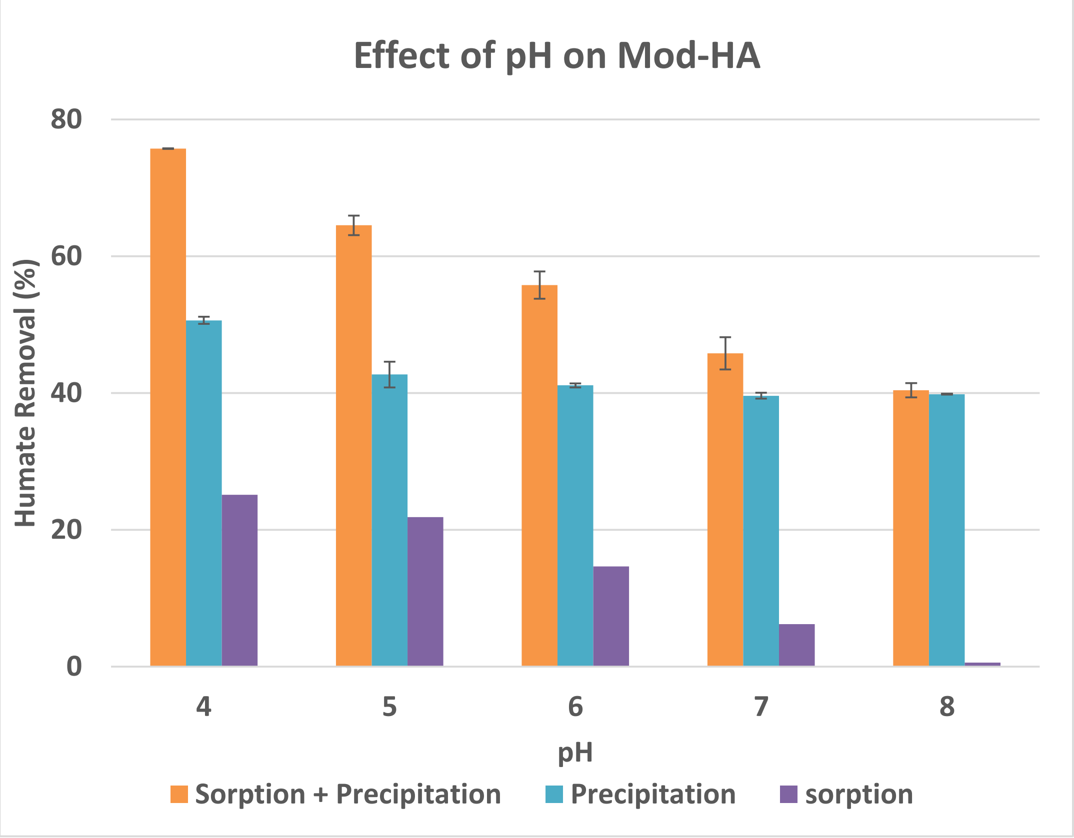
- Determine if the modified humic acid (KW15 modified Humics) can be used to control the mobility of uranium in groundwater and study the sorption/desorption of modified HA on SRS sediment at various pH via batch experiments.
  - Perform batch sorption experiments with humic acid to simulate the creation of a sorbed humate treatment zone in acidic groundwater contaminated with U.
  - Evaluate the effect of contact time (kinetics), pH and initial uranium concentrations.

Task 2.2 - Humic acid batch sorption with SRS soil

FY9 Research Highlights

Effect of pH

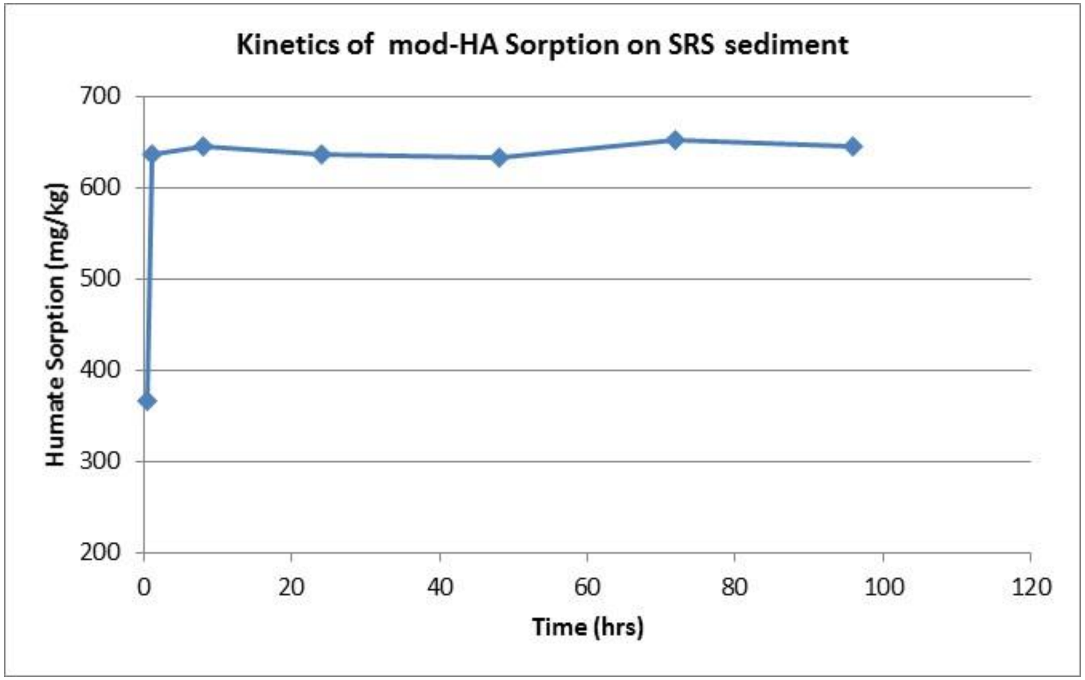
- Completed batch experiment to study the effect of pH (4-8).
- SRS Sediment: 1 g
- Reaction time: 5 Days
- Mod-HA conc: 50 ppm
- With and without sediment
- sorption was calculated from the difference between the total removal and ppt.



Task 2.2 - Humic acid batch sorption with SRS soil
FY9 Research Highlights

Sorption Kinetics

- Mod-HA Conc: 50 ppm
- SRS Sediment: 1 g
- pH 4
- Sampling time: 30 min - 10 days



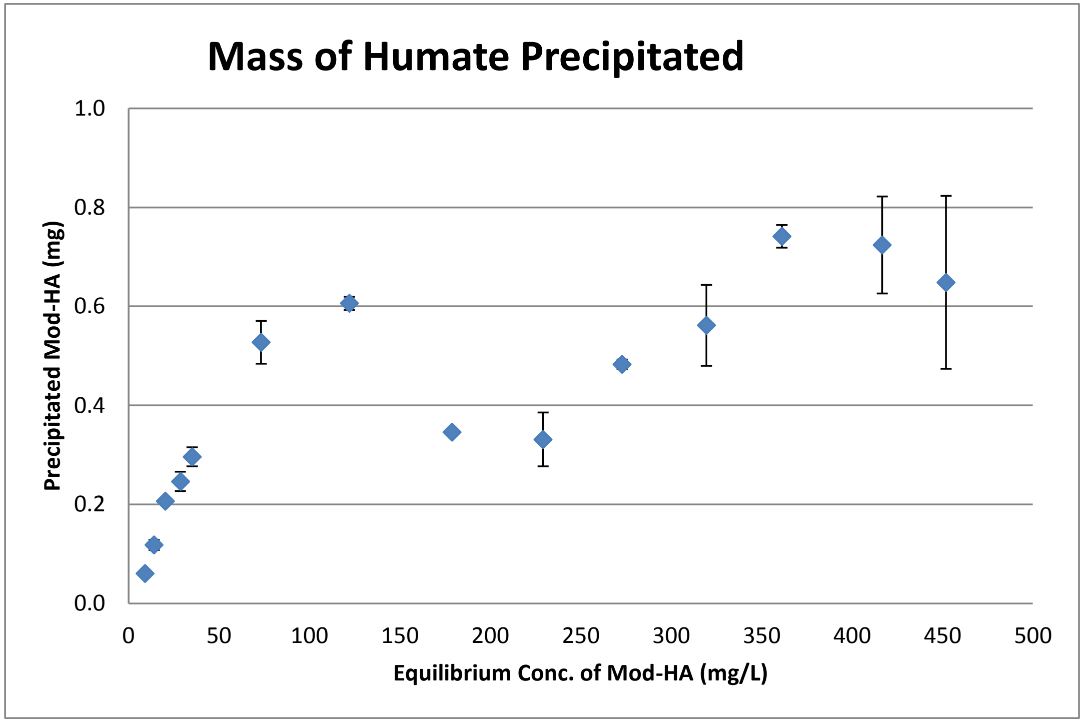
$$q_t = (C_i - C_t)\frac{V}{w}$$

qt = amount of humate adsorbed at time t
Ci = initial concentration of Humate
Ct = concentration of Humate at any time
V = total volume of solution used in the sample
w = weight of SRS sediment in the sample

Task 2.2 - Humic acid batch sorption with SRS soil

FY9 Research Highlights

Equilibrium Studies

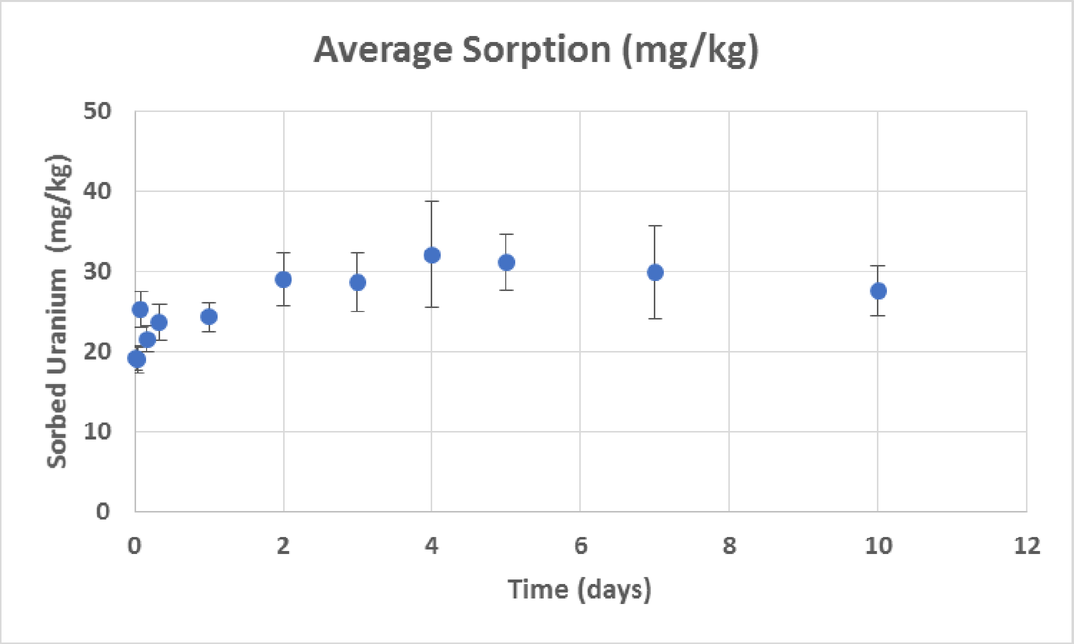


- pH: 4
- Mod-HA Conc: 10 - 500 ppm
- Time: 5 days

Task 2.2 - Humic acid batch sorption with SRS soil

FY9 Research Highlights

Kinetics Studies

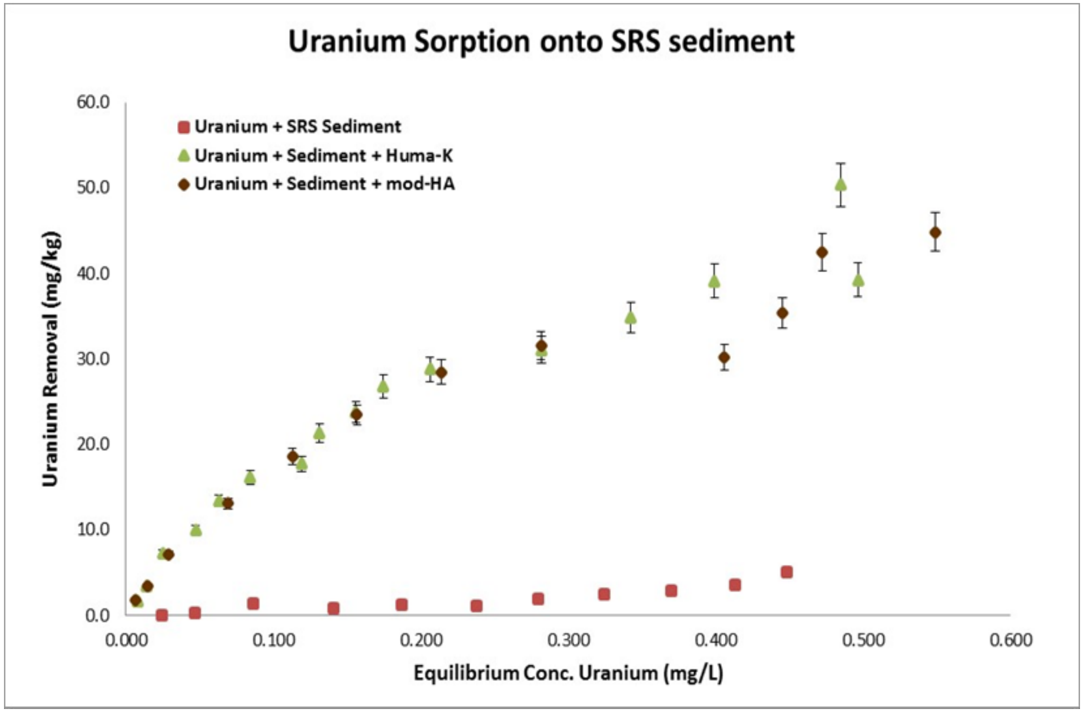


- pH: 4
- SRS Sediment: 200 mg
- Mod-HA Conc: 20 ppm
- Time: 5 days
- Uranium Conc: 0.5 ppm
- Time: 30 mins - 10 days

Task 2.2 - Humic acid batch sorption with SRS soil

FY9 Research Highlights

Equilibrium Studies



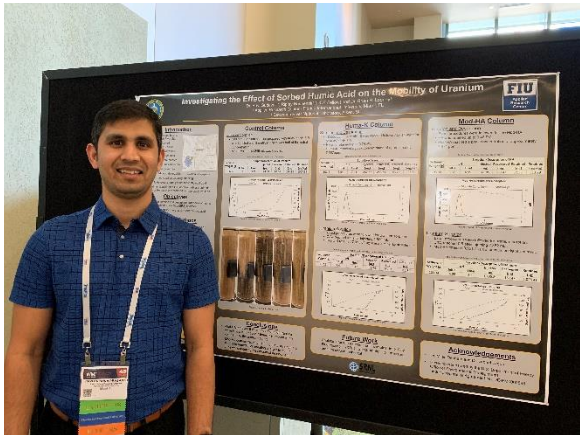
- pH: 4
- SRS Sediment: 200 mg
- Mod-HA Conc: 20 ppm
- Uranium Conc: 0.025 - 1.0 ppm
- Time: 7 days

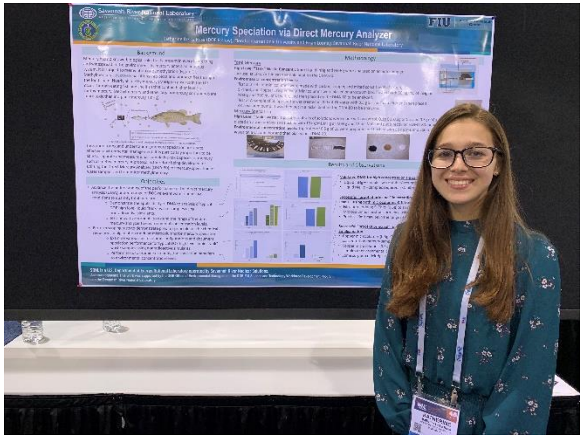
Task 2.2 - Humic acid batch sorption with SRS soil

FY 9 Accomplishments & Future Work

- **Accomplishments for Year 9:**
  - Presented a poster at WM2019.
  - Katherine presented a student poster at WM 2019, LSSF.

- **Objectives for FIU Year 10**
  - Finalize mod-HA sorption studies and to initiate desorption experiments.
  - Study the effect of pH on uranium sorption on SRS sediment coated with mod-HA.

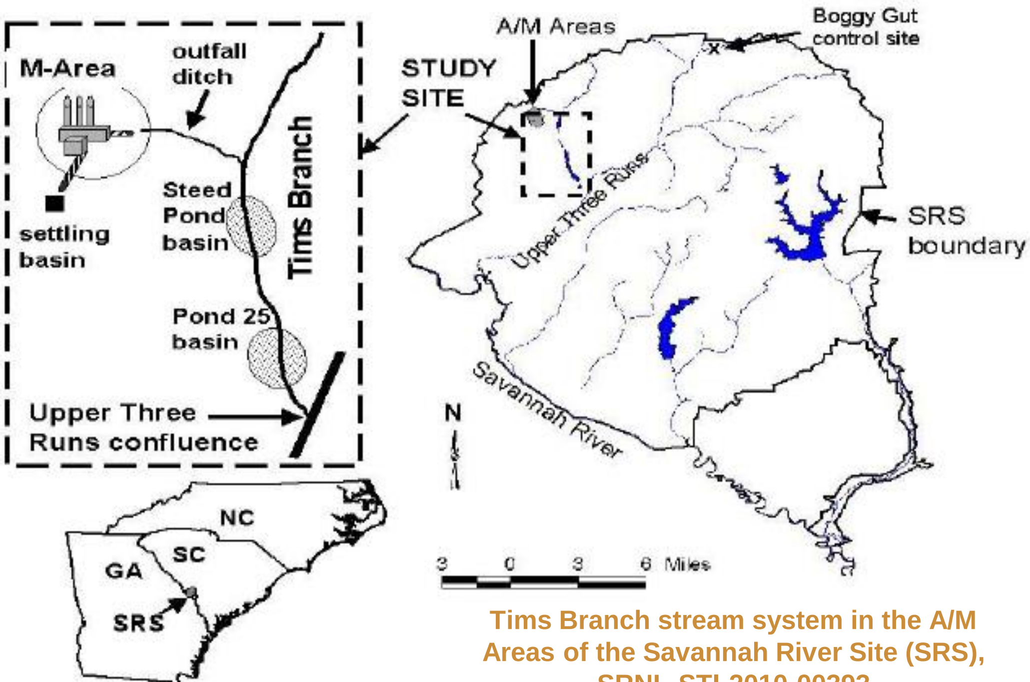




Task 3: Contaminant Fate And Transport Modeling in the Tims Branch Watershed

Background:

- Tims Branch, SRS - small-scale watershed that received contaminant discharge from nuclear research in A/M Area.
- Historical data has shown contaminant migration in surface water/sediment and deposition downstream in ponded areas during heavy rainfall/storm events.
- Full-scale tin (Sn)-based mercury treatment in 2007 using stannous chloride and air stripping eliminated anthropogenic Hg.
- Data on the concentration and timing of the release of the Sn-based treatment has provided a unique opportunity to use Tims Branch as test bed to develop a numerical modeling tool.
- Residual Sn by-products can be treated as conservative tracer to evaluate impacts of extreme hydrological events on fate and transport of major contaminants of concern (e.g., Hg, U, Ni) in Tims Branch.



Tims Branch stream system in the A/M Areas of the Savannah River Site (SRS), SRNL-STI-2010-00393

Task 3: Contaminant Fate And Transport Modeling in the Tims Branch Watershed

Site Needs:

- Heavy metal and radionuclide contamination (e.g. Hg, Ni, U) at SRS and other DOE sites still exists*. Prediction of the fate and transport of these contaminants during severe rainfall/storm events is required as well as long-term monitoring to evaluate the effectiveness of implemented remediation technologies.

Objectives:

- Develop numerical modeling tool to evaluate impact of extreme hydrological events on fate and transport of major contaminants of concern in Tims Branch.
- Develop this tool as a transferable technology potentially applicable in other contaminated stream systems at SRS/other DOE EM sites.
- Collect *in-situ* field data (e.g., flow depth & velocity, suspended particle conc. and other water quality parameters) to support model calibration and validation via in-person sampling and data collection as well as deployment of remote monitoring devices.

Subtasks:

3.1 Modeling of SW Flow & Contaminant Transport in Tims Branch

3.2 Application of Geospatial Tech. for Long-Term Env. Monitoring

3.3 Data Collection, Sampling & Analysis in Tims Branch Watershed

**DOE EM's Technology Plan to Address EM Mercury Challenge & DOE EM's Innovation & Technology Program*

Task 3: Contaminant Fate And Transport Modeling in Tims Branch
FY 9 Research Highlights

FIU Applied Research Center

Tims Branch Hydrology Model Optimization

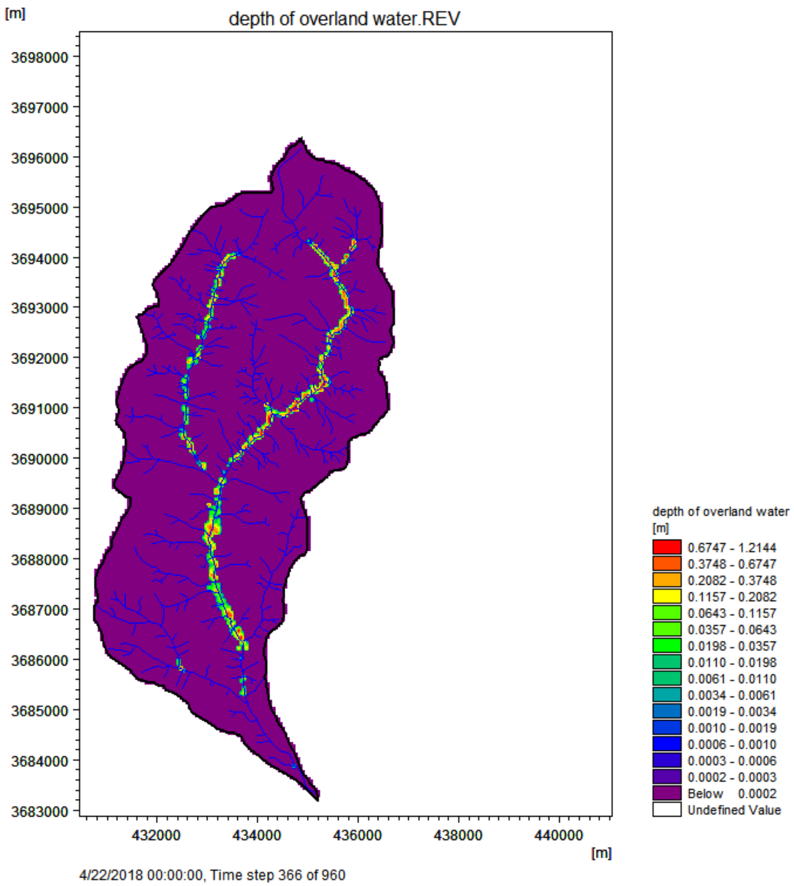
- FY 2017-2018: Coupled MIKE SHE/MIKE 11 hydrology model of Tims Branch watershed developed.
  - 2D land surface/3D subsurface model and 1D stream flow model.
- FY 2018-2019: Enhanced model performance and model representativeness:
  - Monitored streamflow TS prepared to evaluate predicted TS
  - Model inputs updated/diversified (PCP, ET, Veg, Soil, NWK, etc.)
  - Input data properly resampled to model grid (Veg, Soil, DEM, etc.)
  - Databases updated: Veg (LAI, RD, K_c), Soil (ρ_b, K_{sat}, θ_r, θ_s)
  - Parameter optimizations with Autocal tool

Coupled Hydrology & Contaminant Transport Model

- FY 2018-2019: MIKE 11 AD & ECO Lab module activated.
  - Solute transport: advection, dispersion
  - Sediment transport: sedimentation, resuspension
  - Interactions: adsorption, desorption

Continued Remote Data Collection

- FY 2018-2019: Water level/discharge TS data from remote monitoring devices deployed in Tims Branch collected and used for model calibration and validation.



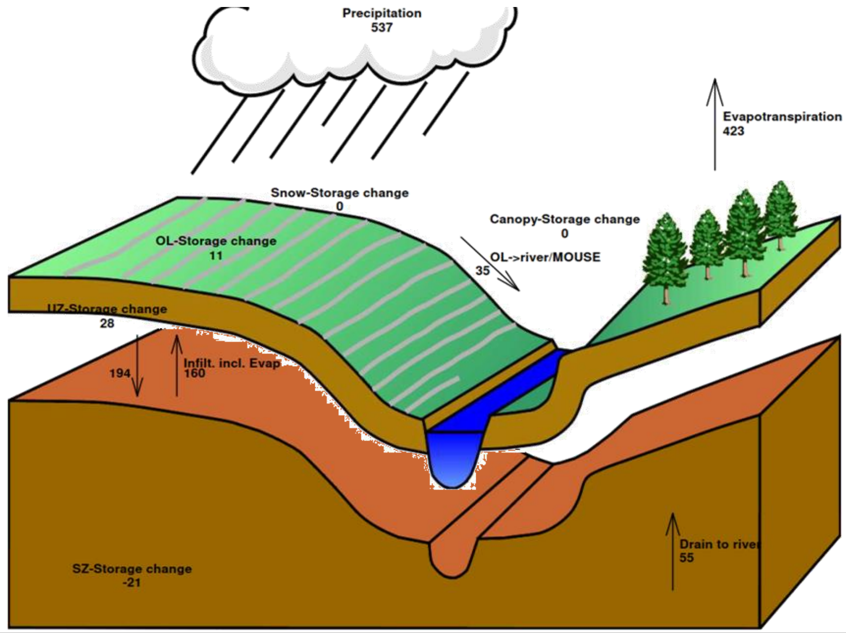
Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FY 9 Research Highlights

MIKE SHE/MIKE 11 Tims Branch Hydrology Model

	Data	Module	Detail
Representativeness	Precipitation	MIKESHE - Climate	Replaced daily precipitation with 15-min averaged TS provided by SRNL Atmospheric Tech. Gp.
	Reference ET	MIKESHE - Climate	Replaced constant ET with daily averaged TS calculated from pan evaporation data provided by SRNL Atmospheric Tech. Gp.
	Vegetation map & database	MIKESHE - Landuse	Updated to latest 2016 map together with corresponding leaf area index, root depth and crop coefficients for 15 vegetation types, collected from National Land Cover Database, USGS
	Soil map & Database	MIKESHE – Unsaturated Zone	Replaced uniform soil distribution with latest 2016 soil map with corresponding bulk density, saturated water content, residual water content and saturated hydraulic conductivity collected from Soil Survey Geographic Database (SSURGO), USDA
Performance	Network	MIKE11 - Network	Replaced dendritic stream network (101 branches) with simplified stream network (5 primary branches). This reduced hydrology model runtime by 4 times and contaminant transport model by 20 times.
	Parameter optimization	MIKESHE/MIKE11	Model optimizations performed by adjusting calibration parameters automatically using MIKE AutoCal tool to achieve best fit between simulated and observed streamflow TS.

Task 3: Contaminant Fate And Transport Modeling in Tims Branch
FY 9 Research Highlights
MIKE SHE/MIKE 11 Tims Branch Hydrology Model



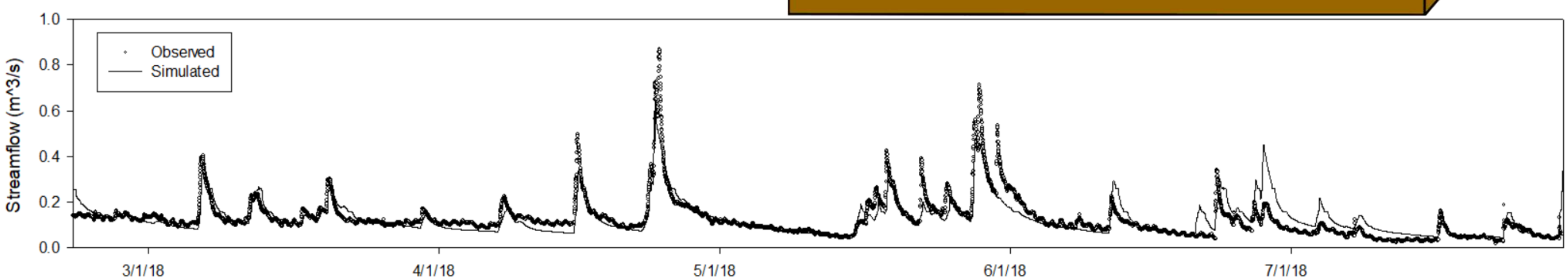
Optimization results

Sensitive parameters:

- MIKE SHE:
  - Drainage level of saturated zone
  - Drainage time constant of saturated zone
  - Horizontal and vertical hydraulic conductivities
  - Overland leakage coefficient
- MIKE 11:
  - Streambed roughness: Manning's M
  - Groundwater leakage coefficient

Optimized model performance:

- Root mean squared error (RMSE): **0.050 cms**
- Nash-Sutcliffe efficacy coefficient (NSE): **0.847**



Current model calibration result contrasting predicted streamflow (solid line) with observed streamflow (circle) for the calibration period of 02/20/2018 to 07/30/2018.

Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FY 9 Research Highlights

Tims Branch Contaminant Transport Model

MIKE11 AD Module

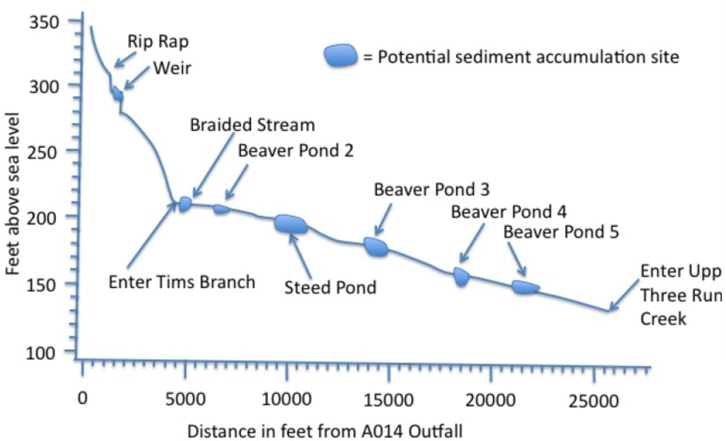
- Solute transport:
  - Advection/Dispersion

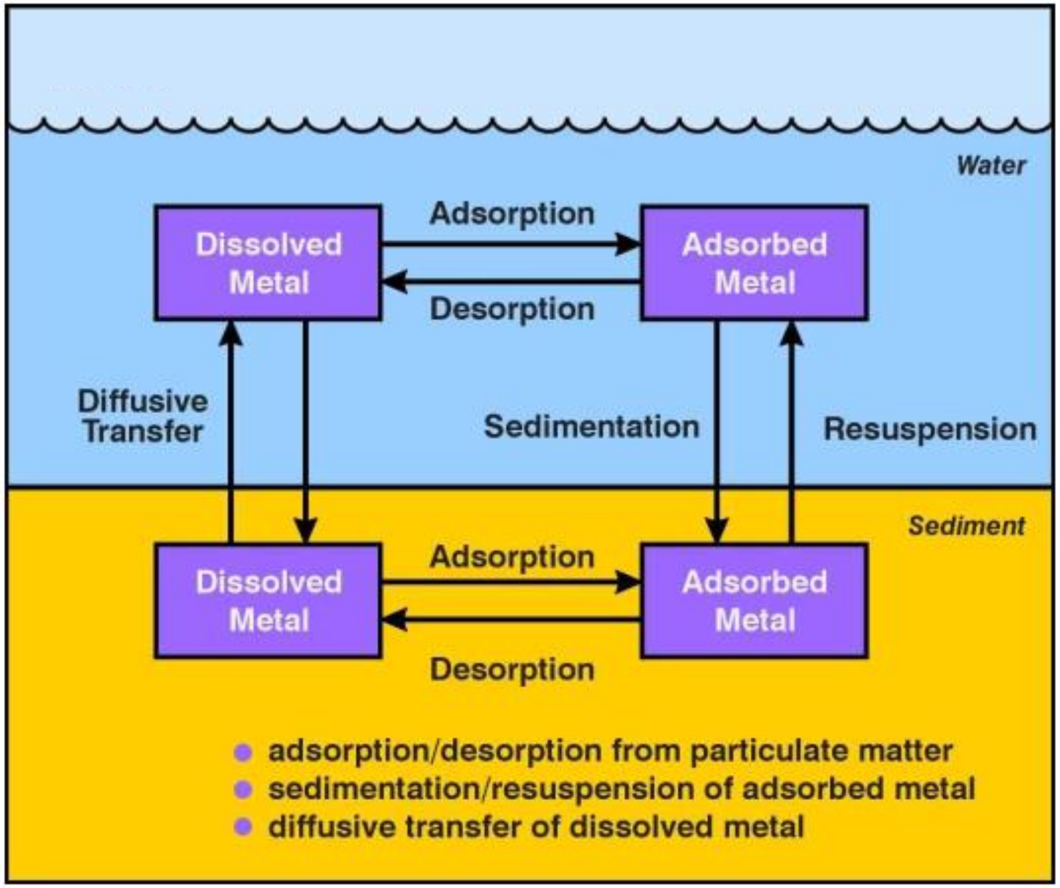
MIKE ECO Lab

- Suspended solid/sediment
  - Sedimentation/Resuspension
- Interactions with heavy metal
  - Adsorption/Desorption
  - Diffusive transfer

Coupling MIKE11/MIKE ECO Lab

- Simplify stream network
- Modifying time step: runtime 80h to 4h





Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FY 9 Research Highlights

Tims Branch Contaminant Transport Model

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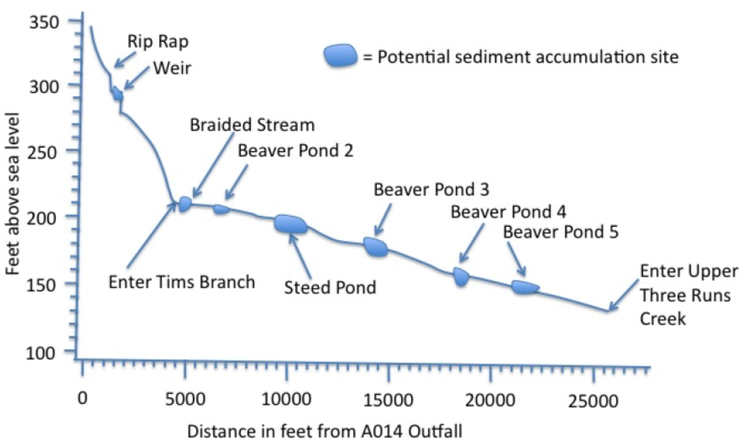

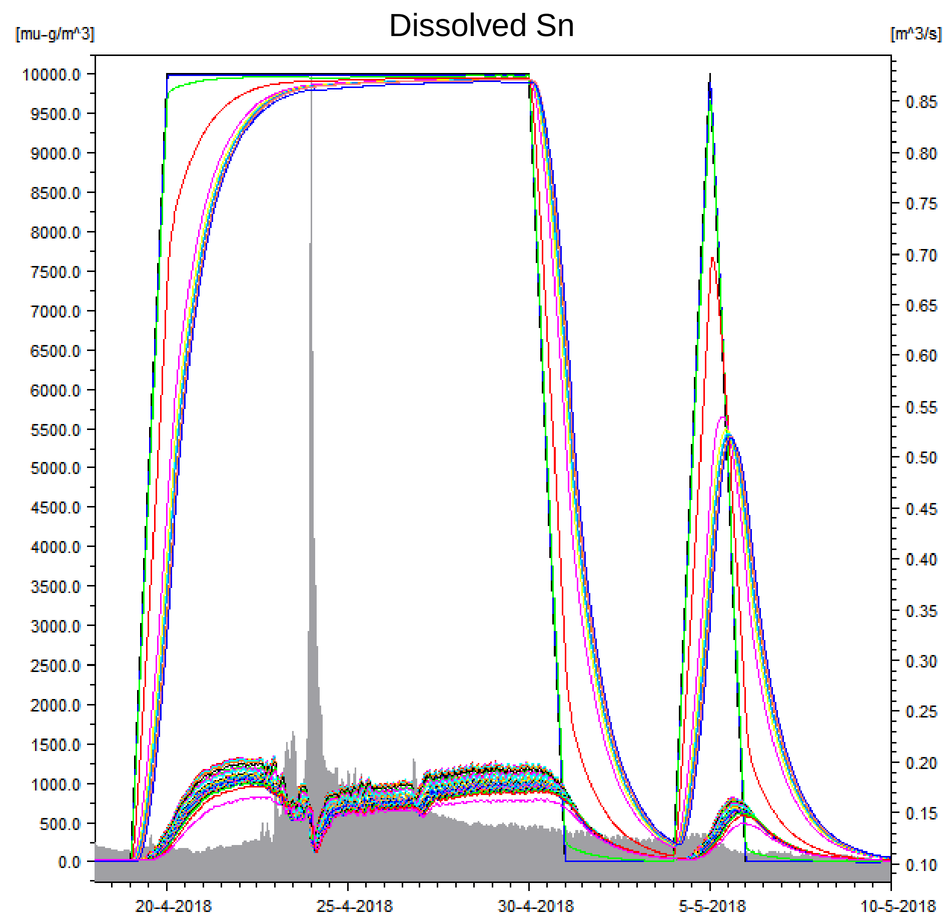

Task 3: Contaminant Fate And Transport Modeling in Tims Branch
FY 9 Research Highlights
Tims Branch Contaminant Transport Model

MIKE11 AD Module
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  - Simplify stream network
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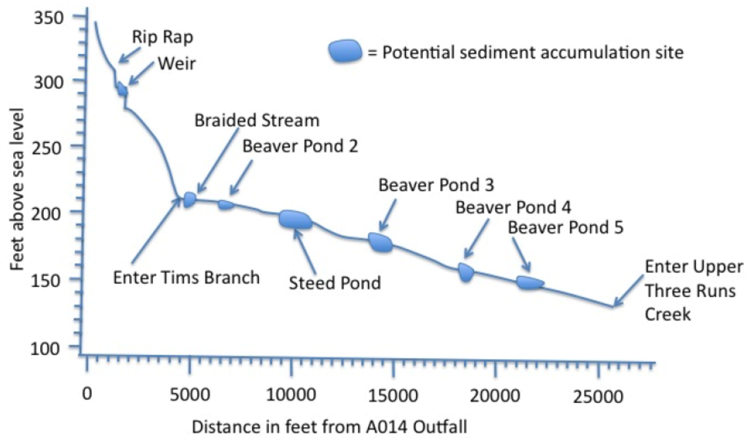

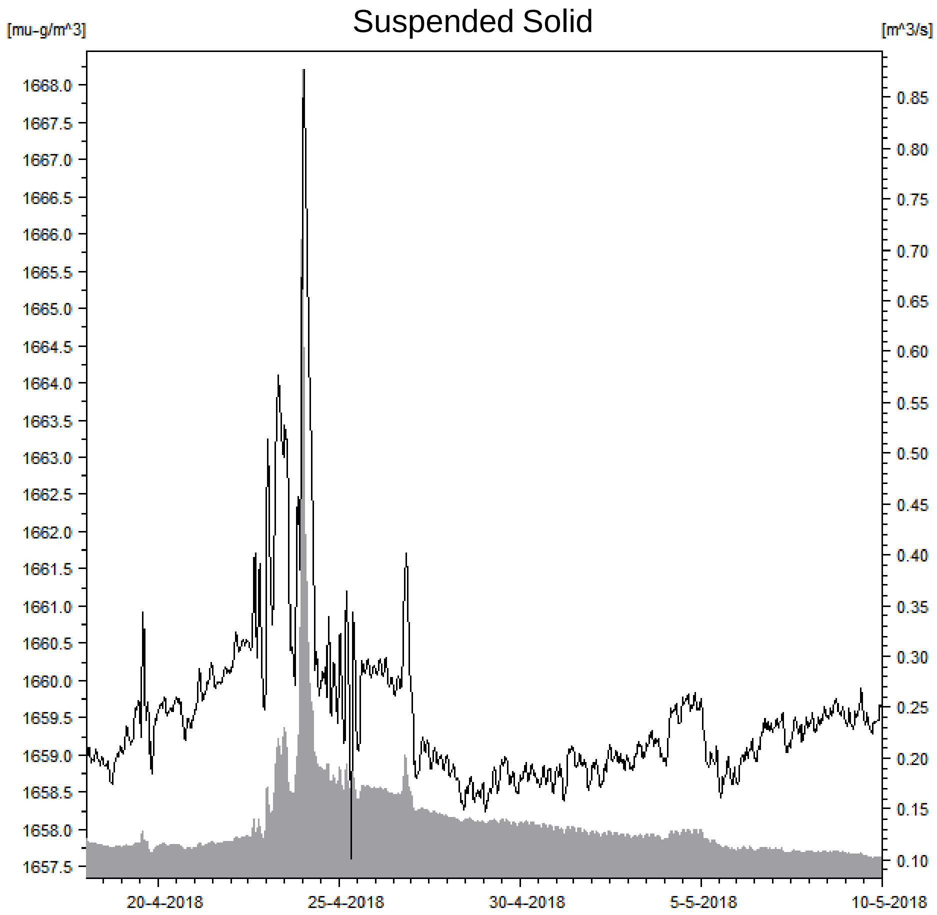

Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FY 9 Research Highlights

Tims Branch Contaminant Transport Model

MIKE11 AD Module

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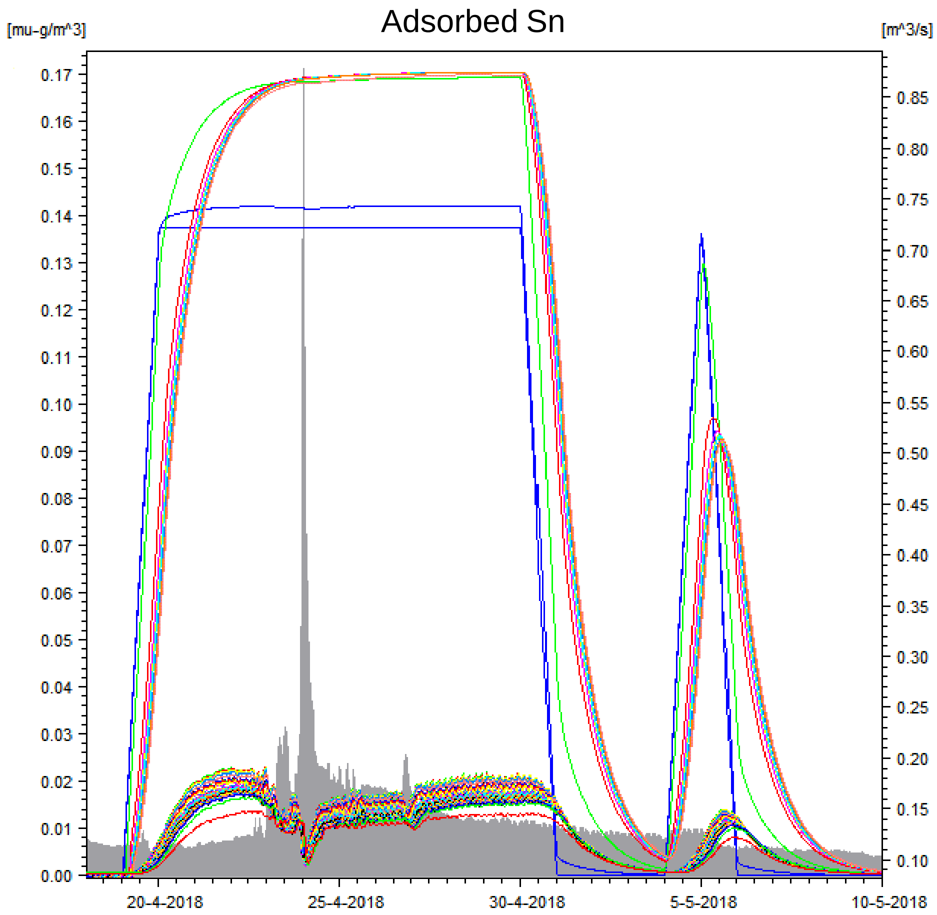
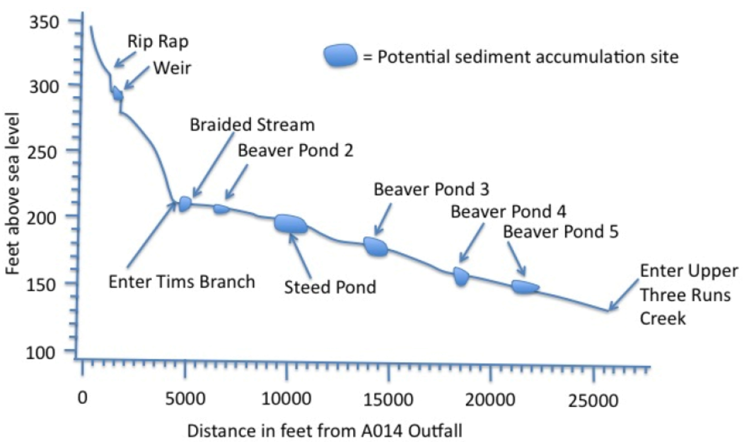




Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FY 9 Accomplishments

- Developed GW model using MODFLOW as part of DOE Fellow Ron Hariprashad's Master's thesis:
  - *"Groundwater/surface water Interaction Along the Tims Branch Watershed, Savannah River Site, SC".*
- WM19 paper & oral presentation:
  - Mahmoudi, M., A. Lawrence. *"An Integrated Hydrological Model for Long-Term Monitoring in Tims Branch Watershed, SC"*, Proceedings of the Waste Management Symposia 2019, Phoenix, AZ, March 2019.
- DOE Fellow Amanda Yancoskie completed 2019 10-wk summer internship with SRNL's Atmospheric Technologies Group under the mentorship of Dr. Grace Maze.
  - *"2D Dam-Break Analysis of L Lake and PAR Pond Dams Using HEC-RAS"*
- DOE Fellow Juan Morales completed 2019 10-wk summer internship at Argonne National Lab with the DOE Office of Science - Office of Biological and Environmental Research's Genomic Science Program under mentorship of Dr. Pamela Weisenhorn.
  - *Investigation of the use of metagenomics to investigate the composition, structure and diversity of microbes in soil contaminated with different levels of heavy metals from Tims Branch system.*

Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FY 10 Objectives

FIU Year 9 Ongoing:

- MIKE 11 ECO Lab heavy metal template dev't for major contaminants of concern (U, Hg & Ni).
- Preliminary simulations of contaminant transport for the various contaminants, troubleshooting of errors and optimization of input parameters to improve model performance.
- Fine tuning of model time step settings to improve reliability of coupled model and runtime efficiency.

Objectives for FIU Year 10:

- Sensitivity analysis, calibration and validation of fully coupled contaminant transport model.
- Scenario analysis under extreme hydrological conditions that provide information related to inter-compartmental transfers, stormflow impacts and downstream transport of priority contaminants of concern (e.g., Hg, U, Ni, and other heavy metals and radionuclides).
- Data collection limited to monitoring and download of water level data from existing remote monitoring devices deployed in Tims Branch watershed for model calibration and validation.
- Travel to SRS to perform routine maintenance and calibration of remote monitoring devices.

Task 5 – Research and Technical Support for WIPP

Site Needs:

This research strives to help the LANL ACRSP team to better understand the long-term fate of the actinide elements in the Waste Isolation Pilot Plant (WIPP). Specifically, the effects of ligands in the waste stream (e.g. EDTA and oxalate) on near field mobility of actinides is still unknown (Dunagan, 2007; Brush, 1990). Complexation constants have been measured for most actinides and lanthanides (Thakur *et al*., 2014; 2015; Borkowski *et al*., 2001). However, their long-term stability and sorption are not yet understood in high ionic strength systems. EDTA is a significant risk factor as it is present in significant amounts in waste and could reach up to 0.3 mM in the repository (Roach *et al.,* 2008).

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 – Research and Technical Support for WIPP

FY 9 Objectives:

To understand the ternary interactions between actinides and WIPP-relevant ligands and minerals and their potential fate in the subsurface.

1. Measure sorption parameters for Nd(III), Th(IV), and U(VI) onto dolomite in variable ionic strength and with and without EDTA
2. Measure sorption parameters for Nd(III), Th(IV), and U(VI) onto dolomite in WIPP-relevant brines, GWB and ERDA-6

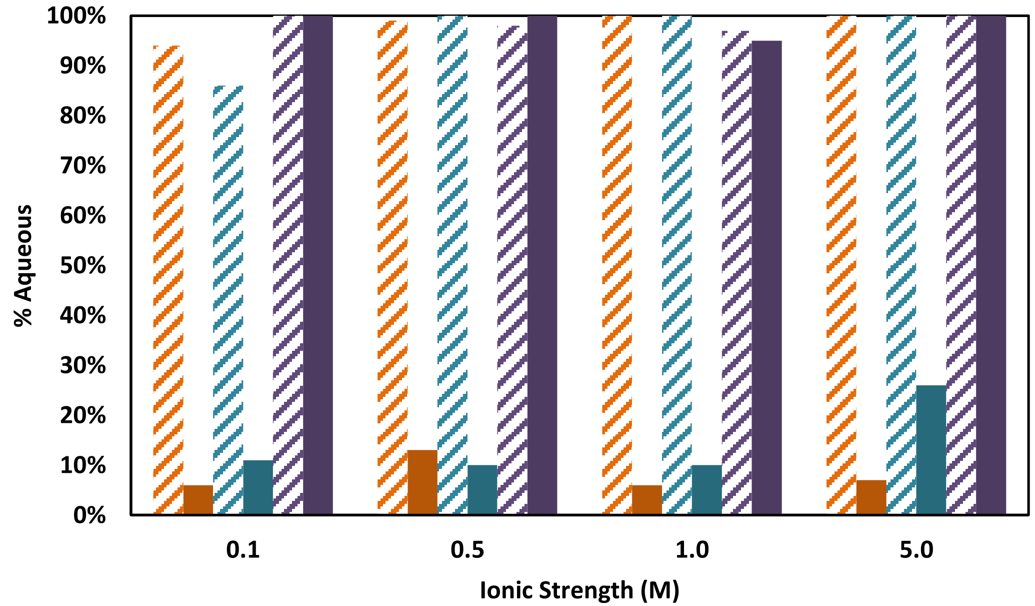
Contaminants	**Brine**	**Dolomite**	**EDTA**	**Concentration**
(ppb)		(g/L)	(mg/L)	(M)
10 Nd, Th, U	NaCl	5	50	0.1
		5	50	0.5
		5	50	1.0
		5	50	5.0
	ERDA-6	5	50	Borkowski et al. (2009)
	GWB	5	50	Borkowski et al. (2009)
1000 Nd, Th, U	NaCl	5	50	0.1
		5	50	0.5
		5	50	1.0
		5	50	5.0
	ERDA-6	5	50	Borkowski et al. (2009)
	GWB	5	50	Borkowski et al. (2009)

Task 5 – Research and Technical Support for WIPP

FY9 Research Highlights

Results highlight effect of ionic strength and EDTA on sorption:

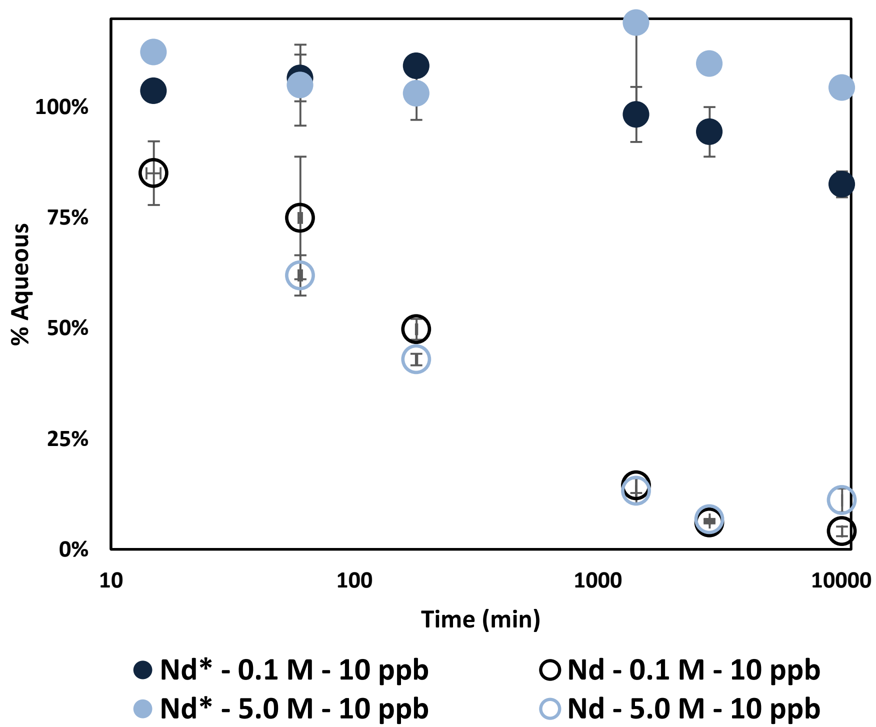
- Finalized batch experiments to investigate effect of ionic strength on sorption of Nd(III), Th(IV), and U(VI) to dolomite (0.1, 0.5, 1.0, and 5.0 M NaCl)
- Investigated effect of EDTA on sorption of Nd(III), Th(IV), and U(VI) to dolomite in variable ionic strength
- Conducted batch experiments in two WIPP-relevant brines, ERDA-6 and GWB (Borkowski *et al*., 2009)



Aqueous fractions of Nd^{3+} (orange), Th^{4+} (blue), and UO_2^{2+} (purple) in variable ionic strength (NaCl) with **(striped)** and without **(solid)** EDTA after 48 hours

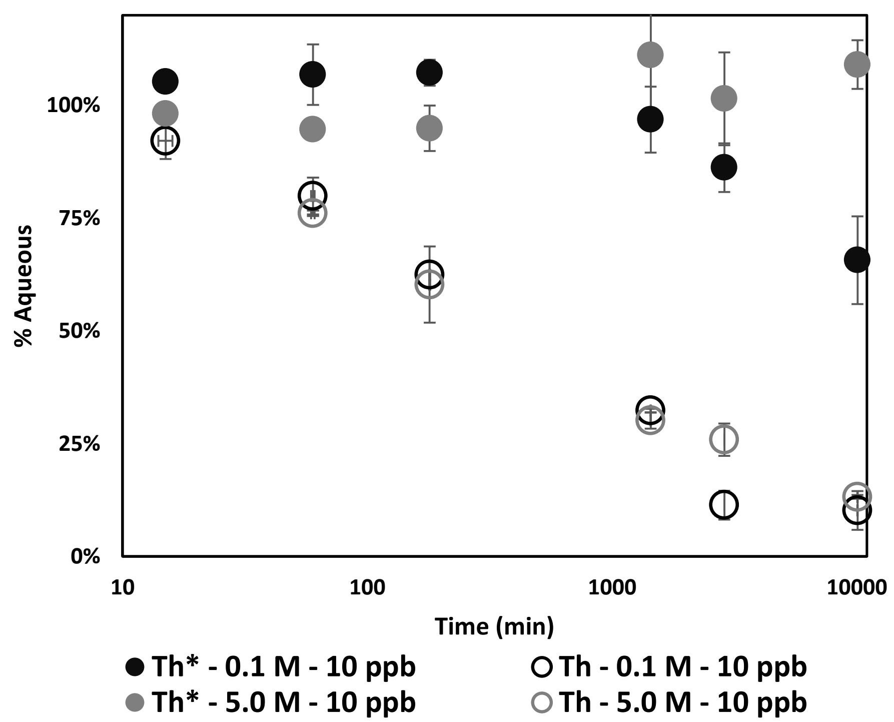
Task 5 – Research and Technical Support for WIPP
FY9 Research Highlights

Aqueous Nd(III) over time in 0.1 and 5.0 M NaCl with (Nd*) and without EDTA



* With EDTA

Aqueous Th(IV) over time in 0.1 and 5.0 M NaCl with (Th*) and without EDTA



* With EDTA

Task 5 – Research and Technical Support for WIPP

FY9 Accomplishments

- Publication titled "Potential for transport of Cesium as a biocolloid in high ionic strength systems" was accepted to *Chemosphere* (May 2019).
- DOE Fellow Frances Zengotita was accepted into the Seaborg Institute Nuclear Science and Security Summer Internship Program at Lawrence Livermore National Laboratory (Summer 2019).
- DOE Fellow Alexis Vento is interning at Sandia National Laboratory with Andy Ward (Summer 2019).
- DOE Fellow Alexis Vento presented on dolomite dissolution in high ionic strength systems at the Mirion Connect 19 Conference (July 2019).

DOE Fellow Frances Zengotita is currently interning at LLNL working with Dr. Enrica Balboni.

Task 5 – Research and Technical Support for WIPP

Upcoming for FY 9:

- Present results on ionic strength effects on sorption of Nd(III), Th(IV), and U(VI) onto dolomite at the Fall ACS national meeting, August 2019
- Visit LANL collaborators to determine direction for future work supporting the WIPP

Objectives for FIU Year 10:

- Expand work scope to investigate the impact of citrate and oxalate on the sorption of contaminants to dolomite in high ionic strength systems via batch and column experiments
- Continue the work with EDTA with mini-column experiments to further investigate the removal mechanisms of Nd(III), Th(IV), and U(VI) in the presence of ligands and high ionic strength systems.

Task 6: Hydrology Modeling For WIPP (New)

Background:

- Federal regulations specify that performance of the WIPP must be predicted based on extrapolating current land-use practices in the vicinity of WIPP to 10,000 years.
- Administrative controls are to be implemented to deter incompatible activities within the Land Withdrawal Act (LWA) boundary.
- Significant changes within the last several years, including increased water withdrawals outside the LWA boundary that have impacted water levels and chemistry in compliance monitoring wells on site.
- Questions about recharge to the Rustler Formation overlaying the Salado Formation that hosts the repository remain unanswered.

Site Needs:

- There is a need for an improved understanding of the regional water balance, particularly the relationship between Culebra recharge and the intense, episodic precipitation events typical of the monsoon.
- This relationship is essential for understanding the rate of propagation of the shallow dissolution front, and the impact of land-use changes around the WIPP facility on water levels in compliance-monitoring wells.
- These types of analyses require a revision of the current site conceptual model to couple surface water and groundwater processes, which both require a high resolution DEM including channels and sink holes to account for surface water routing and return flow.

Task 6: Hydrology Modeling For WIPP (New)

FIU Applied Research Center

Objectives:

- Development of a GWM for the WIPP site using the DOE-developed Advanced Simulation Capability for Environmental Management (ASCEM) modeling toolset to improve the current understanding of regional and local groundwater flow at the WIPP site.

- An open source LSM will also be used to provide surface process parameters for input into the ASCEM model (e.g. infiltration rate) to compute the surface water balance, across multiple scales and reduce uncertainties in recharge estimates and propagation of the shallow dissolution front.

Subtasks:

6.1 Digital Elevation Model (DEM) and Hydrologic Network
- High-res DEM needed to delineate and extract topographical features such as drainage basins, brine lakes, channels, sink holes, discharge points and other relevant hydrological features for input into selected LSM to model terrestrial overland flow, channel routing, and subsurface flow processes.

6.2 WIPP Hydrologic Database Development
- Central data repository (geodatabase) & use of geospatial tools for processing model input data

6.3 ASCEM GWM and LSM Training
- Training of FIU personnel/students on ASCEM modeling toolset using existing case studies of ASCEM implementation at DOE sites to determine best practices/lessons learned for similar implementation at WIPP.
- Understand requirements for coupling state-of-the-art LSM with a variably saturated ASCEM GWM.

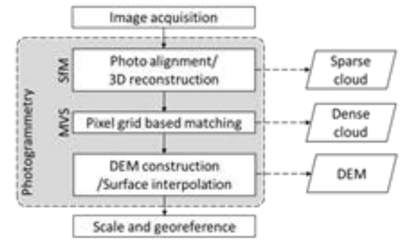
Task 6: Hydrology Modeling For WIPP (New)

Research Highlights

Subtask 6.1: DEM and Hydrologic Network

Literature Review

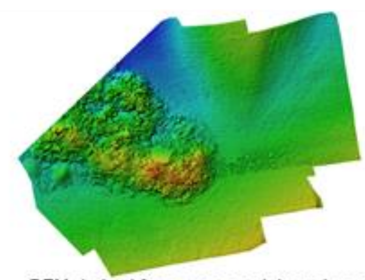
- Methods for development of a high-resolution DEM.
- Methods for extracting surface features (sink holes, hydrology network etc.) from LiDAR-derived DEMs.



Photogrammetry Test

- Data acquisition test conducted in small field beside ARC parking lot using drone with 12 MP digital camera.
- Images processed using photogrammetry software to generate a high-res DEM (5 mm/pixel).
- This method can generate sub-meter accuracy DEMs for LSM development.


Dense cloud generated from drone image


DEM derived from processed drone image

Training of DOE Fellows on geospatial data & drone image processing techniques

- Watershed delineation from DEM using ArcHydro tools with the ArcGIS/ArcMap platform.

Task 6: Hydrology Modeling For WIPP (New)

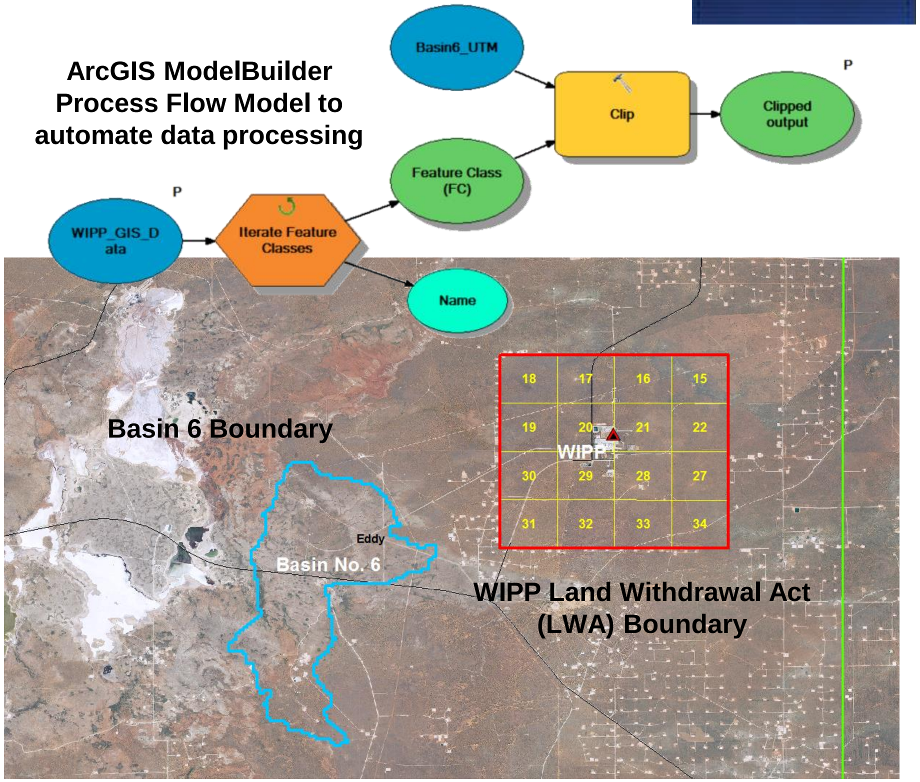
Research Highlights

Subtask 6.2: WIPP Hydrologic Database

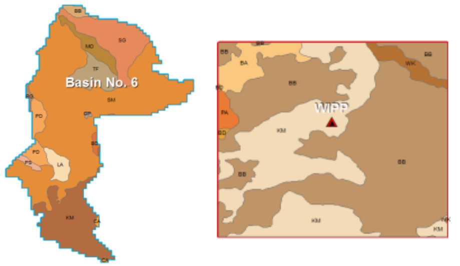
- Data mining/download of spatial/temporal data
  - DEMs, hydro networks, water bodies, basins, geology, soils, vegetation/land cover, roads, admin. boundaries.
  - Students trained to use Python scripts to automate download of large datasets and reduce task timeframe.
- Federal/state/local online databases
  - USGS (NHD), USDA (NRCS - SSURGO/STATGO), MRLC Consortium (NLCD), NM State, CFO.
- ArcGIS geodatabase as central data repository
- Data had varying spatial extents (county/state/CONUS)
  - Students trained on dev't of process flow models using ArcGIS ModelBuilder for automation of repetitive geoprocessing tasks (e.g. clipping to established spatial extents, projecting to approp. coord. system).
- WIPP/CBFO collaborators - acquire relevant background info and identify knowledge gaps w.r.t. WIPP region's land surface hydrology.

Subtask 6.3: ASCEM GWM and LSM Training

- Delayed – ASCEM team awaiting authorization for funding to prepare short training course. Projected for August/Sept. 2019 or FIU Performance Year 10.



Soil types in Basin 6 *(left)* and within the WIPP LWA boundary *(right)*



Task 6: Hydrology Modeling For WIPP (New)
FY 10 Objectives

FIU Year 9 Ongoing:

- Trip to WIPP/Basin 6 planned in August 2019 to survey study area, meet with collaborators, present project progress and discuss plans for next year.

Objectives for FIU Year 10:

- Pilot study to capture high-res imagery of representative basin at WIPP in Nash Draw area using UAV (drone).
- Image processing using state-of-the-art photogrammetric techniques to build a high-res DEM for accurate delineation/extraction of topographical and hydrologic features.
- Utilize selected open-source LSM, delineated features and other relevant hydrological data collected to initiate development of a LSM of Basin 6, to be used in future to force ASCEM GWMs to predict GW flow patterns.
- Spatial distribution of recharge, and GW flow rates and directions will be used to estimate rate of halite dissolution and rate of propagation of the shallow dissolution front, which both have potential to affect post-closure repository performance.
- Pilot study will serve as proof of concept that the proposed methodology is feasible and has practical applications at WIPP to generate high-res imagery for development of a DEM, which is essential for detailed delineation of hydrologic basins within and surrounding the WIPP Land Withdrawal Act (LWA) boundary.
- Training of FIU's research personnel and students on selected LSM and ASCEM to carry out proposed scope.