DOE-FIU Cooperative Agreement Annual Research Review – FIU Year 3

Wednesday, August 23, 2023		
9:00 - 9:05 am EDT	Kick-Off /Welcoming Remarks (DOE-EM)	Rod Rimando (Acting Director, Technology Development) – DOE EM-3.2
9:05 - 9:10 am EDT	Welcoming Remarks (DOE-LM)	Ms. Jalena Dayvault (Site Manager) – DOE LM
9:10 - 10:40 am EDT	Project 2: Environmental Remediation Science & Technology	FIU, DOE HQ, SRNL, PNNL, ORNL, LANL, LBNL, CBFO
10:40 am - 12:10 pm EDT	Project 1: Chemical Process Alternatives for Radioactive Waste	FIU, DOE HQ, PNNL, WRPS, SRNL, SRS
LUNCH BREAK [12:10 – 1:30 pm]		
1:30 - 3:00 pm EDT	Project 3: Waste and D&D Engineering & Technology Development	FIU, DOE HQ, SRNL, PNNL, LBNL, INL, ANL
Thursday, August 24, 2023		
9:00 - 10:30 am EDT	Projects 4 & 5: STEM Workforce Development and Training	FIU, DOE HQ (EM & LM), SRNL, PNNL, WIPP, SRS, ORP, LBNL, WRPS, INL, Grand Junction
BREAK [10:30 – 10:35 am]		
10:35 - 12:00 pm EDT	Wrap Up (FIU Projects 1, 2, 3, 4 & 5)	FIU, DOE HQ (EM & LM)

PROJECT 2

Environmental Remediation Science & Technology

FIU Personnel and Collaborators

Principal Investigator: Leonel Lagos

Project Manager: Yelena Katsenovich

Faculty/Staff: Ravi Gudavalli, John Dickson, Vadym Drozd, Angelique Lawrence, Pieter Hazenberg

**DOE Fellows/Students: ***Angel Almaguer, *Kirsten Olson, Hannah Aziz, *Stevens Charles, Mariah Doughman, *Caridad Estrada, Aubrey Litzinzer, *Phuong Pham

DOE-EM: Genia McKinley, *Kurt Gerdes, Rod Rimando, Skip Chamberlain, Nick Machara, *Karen Skubal, Alexander Koenig

DOE-SRS: Phillip (Tony) Polk

SRNL: Brian Looney, Hansell Gonzalez-Raymat, Carol Eddy-Dilek, Mark Amidon, Bruce Wiersma, Connie Herman, Brady Lee

SREL: Daniel Kaplan

LBNL: Haruko Wainwright, Zexuan Xu

PNNL: Rob Mackley, Nik Qafoku, Jim Szecsody, Hilary Emerson, Matthew Asmussen

DOE-ORP: Erik Nelson

LANL: *Don Reed, Juliet Swanson, David Moulton, Jay Je-Hun Jang, Jean-Francois (Jef) Lucchini.

DOE-CBFO: Anderson Ward

ORNL: Eric Pierce, Alexander Johs

*Former contributors

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Project Tasks and Scope

TASK 1: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE HANFORD SITE	
Subtask 1.2	Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants
Subtask 1.3	Eval. of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments
Subtask 1.4	Experimental Support of Lysimeter Testing
Subtask 1.5	Remediation Research on Combination of Reduction and Sequestration Treatment (NEW)
TASK 2: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE SAVANNAH RIVER SITE	
Subtask 2.1	Investigate Environmental Factors Controlling the Attenuation and Release of Iodine in the Wetland Sediments at Savannah River Site
Subtask 2.2	Investigating the Effect of KW-30 (Humate Material) on the Removal of Comingled Contaminants
TASK 3: CONTAMINANT FATE AND TRANSPORT MODELING FOR THE SAVANNAH RIVER SITE	
Subtask 3.1	Calibration of the Tims Branch Watershed Model and Scenario Analysis
Subtask 3.2	Model Development for Fourmile Branch with Specific Focus on the F-Area Wetlands
TASK 5: RESEARCH AND TECHNICAL SUPPORT FOR WIPP	
Subtask 5.2	Fate of Actinides in the Presence of Ligands in High Ionic Strength Systems
TASK 6: HYDROLOGY MODELING OF BASIN 6 OF THE NASH DRAW NEAR THE WIPP	
Subtask 6.2	Model Development
Subtask 6.3	Fieldwork and Data Collection to Support Hydrological Model Calibration and Validation (NEW)
TASK 7: ENGINEERED MULTI-LAYER AMENDMENT TECHNOLOGY FOR HG REMEDIATION ON OAK RIDGE RESERVATION	

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Task 1

Remediation Research and Technical Support for the Hanford Site

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Subtask 1.2: Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

Site Needs:

- Subtask supports evaluation of potential *in situ* treatment technologies for the vadose zone, groundwater and perched water zone located within the 200 Area at Hanford. This research evaluates re-oxidation behavior of ^{99}Tc in the presence of other co-contaminants (e.g., ^{238}U and nitrate) after initial immobilization via reduction. The results from these batch experiments will be used to determine the extent of Tc remobilization in the presence of co-contaminants and provide insights for remedial actions.

Objectives:

- To study re-oxidation behavior of perched (PW) and groundwater (GW) contaminants, such as $^{99}Tc^{(VII)}$, in the presence of ^{238}U, and NO_3^-, that have been initially reduced by strong reductants such as ZVI, SMI and CPS in batch-scale experiments under anaerobic initial conditions followed by aerobic conditions. Sediment samples that evaluated in these experiments include ^{99}Tc comingled with uranium and nitrate.

Subtask 1.2: Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

FIU Year 3 Research Highlights & Accomplishments:

- Studied re-oxidation behavior of ^{99}Tc, U(VI), and NO_3^- after treatment with strong reductants:
  - 0.5 % calcium polysulfide (CPS) and
  - 5 % CPS

    CPS is a 29% solution.
- Ringold Formation sediment <2 mm in triplicate samples
- Two phases of experiments for reduction of ^{99}Tc, U(VI), and NO_3^-:
  - In presence of CPS under anaerobic conditions for up to **30 days**
  - In aerobic conditions for up to **41 days with aeration 2x/week for 30 s**.

  Total testing = 71 days.
- Measured pH, ORP, DO, Tc, U, NO_3^-, SO_4^{2-} concentrations at each sample point.
- Test matrix:
  - Prepared synthetic solutions of GW and PW
  - Purged with N_2, pH adjusted, and spiked with ^{99}Tc, U(VI), and NO_3^-
  - PW: pH 8.2, 10 µg/L Tc, 150 mg/L U.
  - GW: pH 7.8, 420 µg/L Tc, 124 mg/L NO_3^-
- Phase 1:
  - DO: ~0.03-0.05 mg/L
  - ORP: -300 mV -350 mV indicative of reducing conditions.
- Phase 2: DO and ORP increased:
  - DO: 5-6 mg/L
  - ORP: +150 to +400 mV consistent with oxidative conditions.

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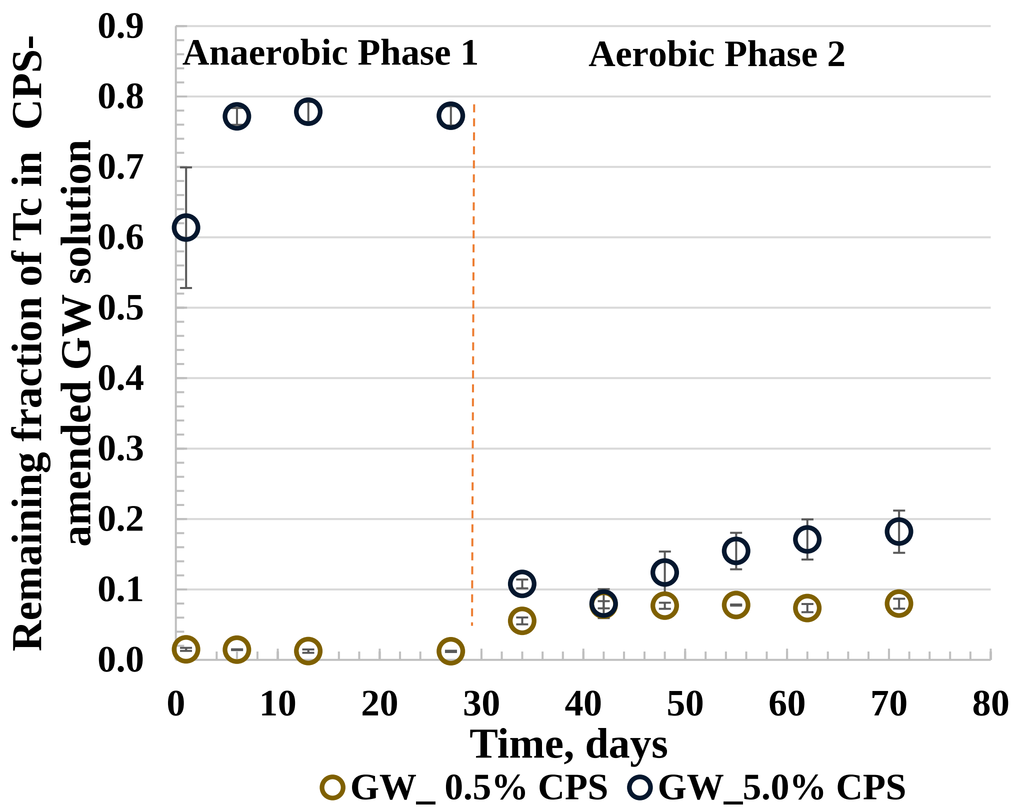
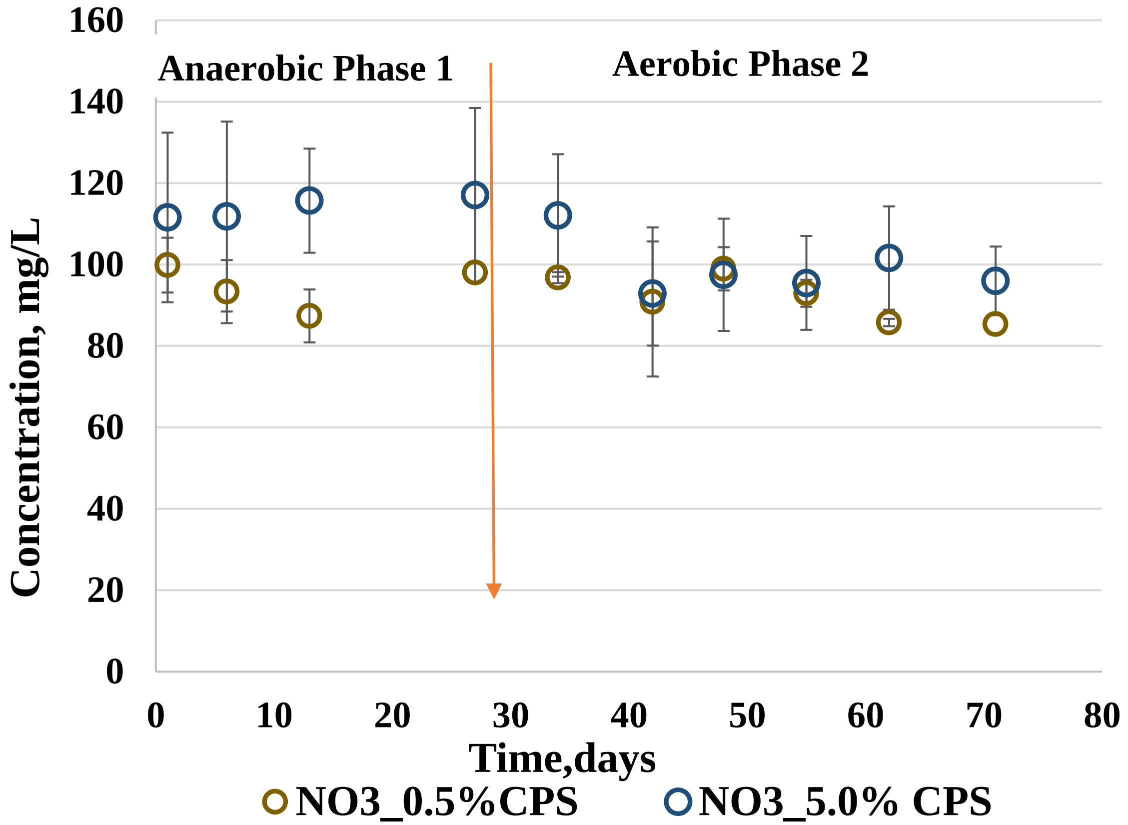
Subtask 1.2: Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

FIU Year 3 Research Highlights & Accomplishments:

Remaining Tc Fraction in GW, 0.5 & 5.0 % CPS



NO_3^- concentrations in GW, 0.5% & 5.0 % CPS



- 0.5% CPS samples contained smaller remaining fraction of Tc(VII) throughout both phases vs. 5.0% CPS.
- There is not much difference in the removal of NO_3^- by 0.5% CPS throughout both phases vs. 5.0% CPS. The NO_3^- removal was >71% and no reoxidation. Additional optimization is needed to improve NO_3^- removal by CPS.

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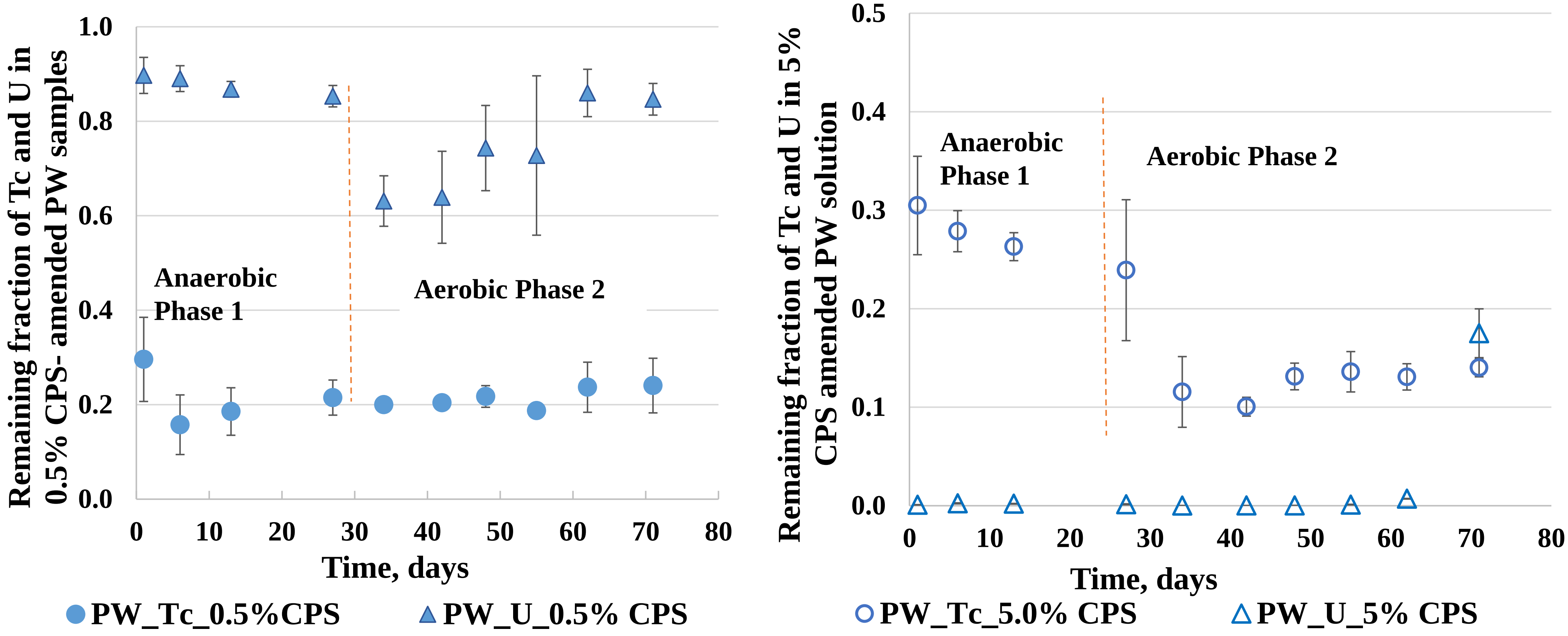
Subtask 1.2: Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

FIU Year 3 Research Highlights & Accomplishments:

Remaining U & Tc Fractions in PW, 0.5 % CPS



- Removal of Tc was similar in 0.5% and 5% CPS samples; however, Tc conc. was higher compared to 1% ZVI.
- U removal with 0.5% CPS showed 0.85±0.03 remaining fraction, while 5.0% CPS improved to 0.17±0.03.

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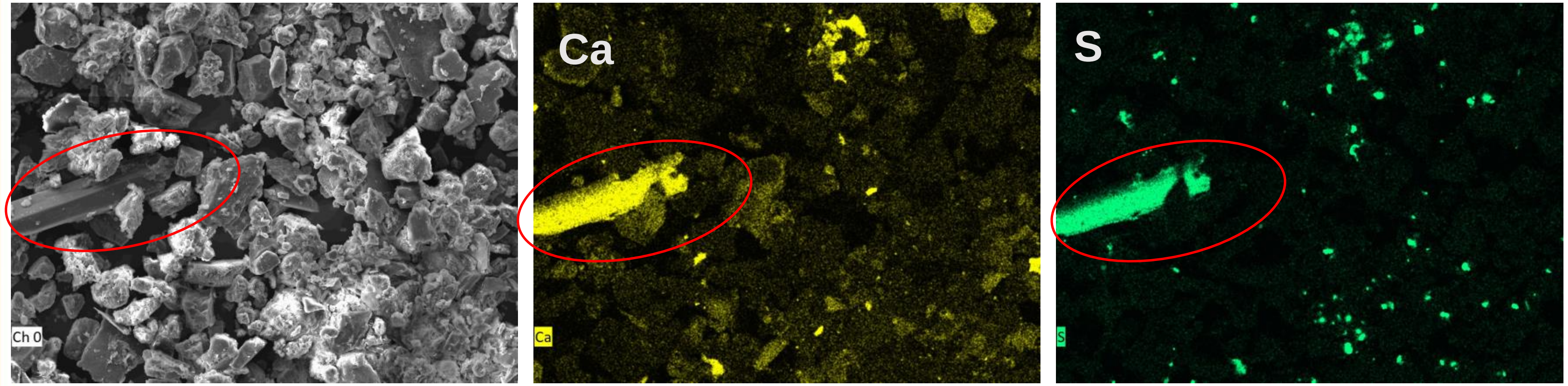
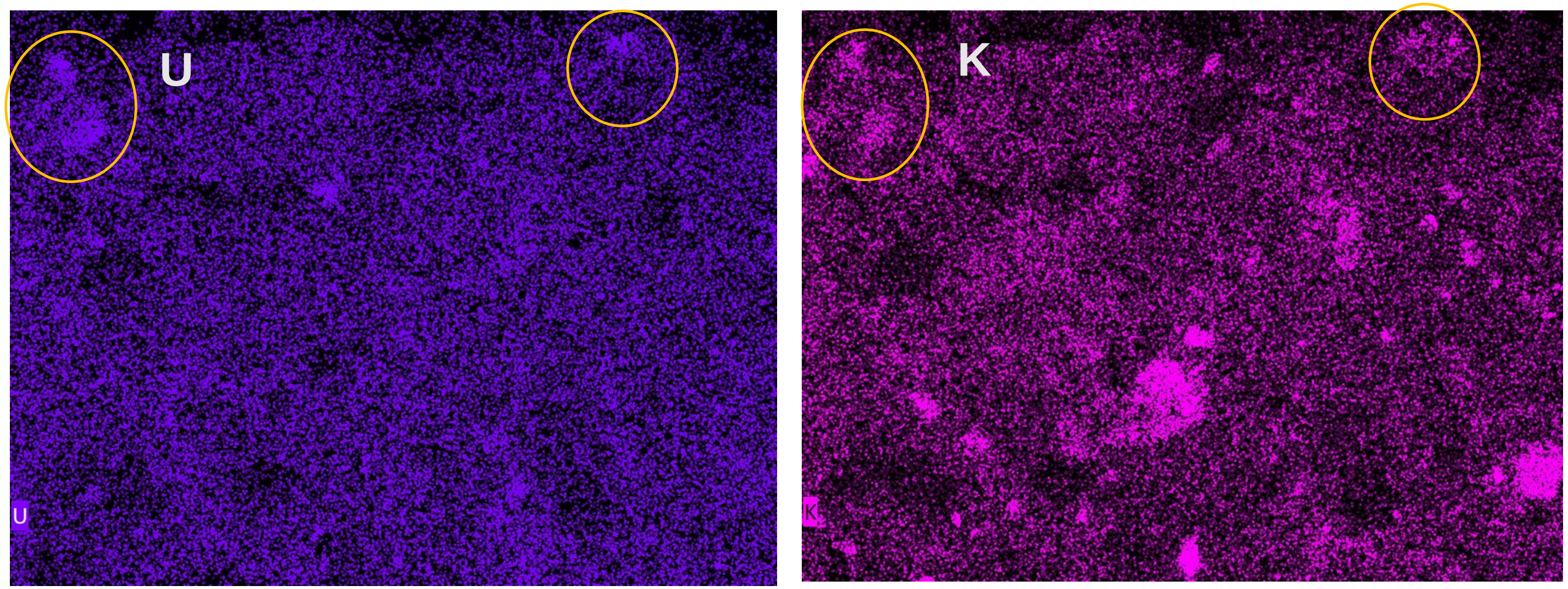
Subtask 1.2: Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

SEM/EDS results



PW 0.5% CPS-amended samples



PW samples**: U** is on a background level, partial alignment with **K**

XRD major solid phases: Quartz, illite, feldspar, albite, vermiculite, nontronite, sulfur

Subtask 1.2: Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants

FIU Year 3 Research Highlights & Accomplishments:

- Completed a study on the re-oxidation behavior of perched and groundwater contaminants, Tc(VII), U(VI), and NO_3^-, that have been initially reduced by 0.5% and 5% calcium polysulfide (CPS) under anaerobic initial conditions followed by aerobic conditions.
- Conducted solid characterization studies via XRD and SEM-EDS to investigate for changes in sediment mineralogy, surface morphology and elemental composition.
- Oral presentation at WM2023 Symposia: "*Re-oxidation Behavior of Technetium-99 and Uranium Immobilized by Strong Reductants*".
- Undergraduate students working on this subtask:
  - **Jonathan Williams** (results on Tc reoxidation in the presence of 0.1%, 1% ZVI and SMI, 0.5% and 5.0% CPS;
  - **Angel Almaguer**- Tc reoxidation behavior in the presence of U(VI) and NO_3^- via 0.1% and 1% ZVI and SMI;
  - **Kirsten Olson**- Tc reoxidation behavior in the presence of U(VI) and NO_3^- via 0.5% and 5.0% CPS.

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FIU Year 4 Projected Scope

- Results indicate 1% ZVI or SMI were stronger reductants under anaerobic conditions and showed better resistance to re-oxidation in aerobic conditions, compared to 0.1% and 0.5% or 5%-CPS- amended PW and GW.
- Initiate preliminary experiments on coupling ZVI approach with ammonium hydroxide and investigate their effect on the re-oxidation behavior of comingled Tc, U and nitrate. Experiments will be conducted under the subtask 1.5.
    - Research will follow experimental matrix outlined in DV-1 Operable Unit treatability study ongoing at Hanford Site.

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Subtask 1.3: Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

Site Needs:

Contaminants (U (VI), ^{129}I, Cr(VI) and NO_3^-) that were released to the environment can potentially impact groundwater. Once active remediation is completed, a transition to monitored natural attenuation (MNA), is needed. Effective MNA requires a thorough understanding of the contaminant immobilization processes that keep the contaminants stable and resistant to remobilization due to changes in environmental conditions or GW chemistry.

Objectives:

Evaluate attenuation processes that affect fate and transport mechanisms of contaminants of concern present in VZ sediment collected from the Hanford Site.

- Conduct competitive adsorption and column experiments on sediment ($\leq$2 mm) with key contaminants of concern at variable molar ratios at Hanford 200 Area GW when all contaminants are commingled together to compare adsorption results when each contaminant is present separately.

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Subtask 1.3: Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

FIU Year 3 Research Highlights & Accomplishments:

Column Methodology

- Hanford formation sediment ≤ 2 mm
- Flow rate: 0.25 mL/min
- 1-hour residence time
- U and Cr and U alone for a total of ~32 pore volumes
- AGW for a total of ~100 pore volumes
  - 16 hours at ~ 4 pore volumes: adsorbed U
  - 144 hours at ~ 11 pore volumes: U from carbonate dissolution
  - 192 hours at 100 pore volumes: U from phosphate dissolution
- 5 pore volumes of AGW
- Repeated Br^- tracer
- Aqueous U and Cr by ICP-MS every 5 samples and Br^- by IC

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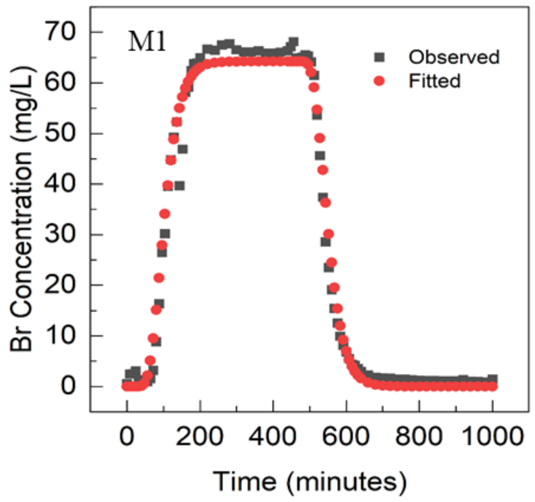
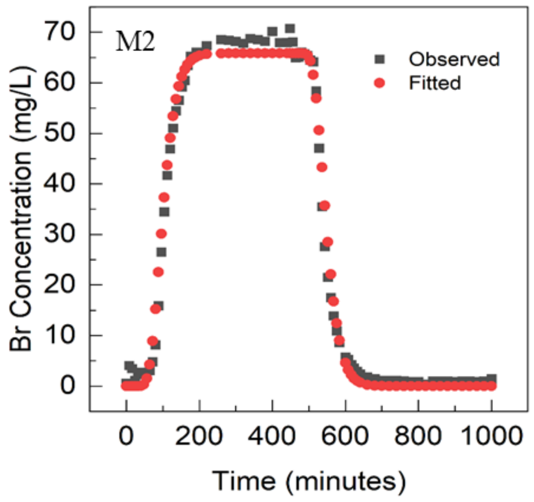
Subtask 1.3: Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

FIU Year 3 Research Highlights & Accomplishments:

Bromide Breakthrough Curves

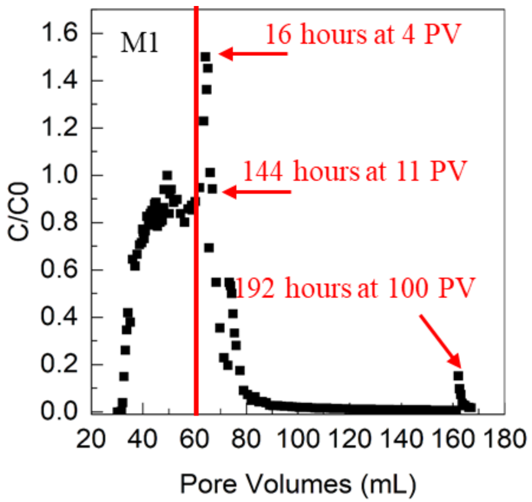


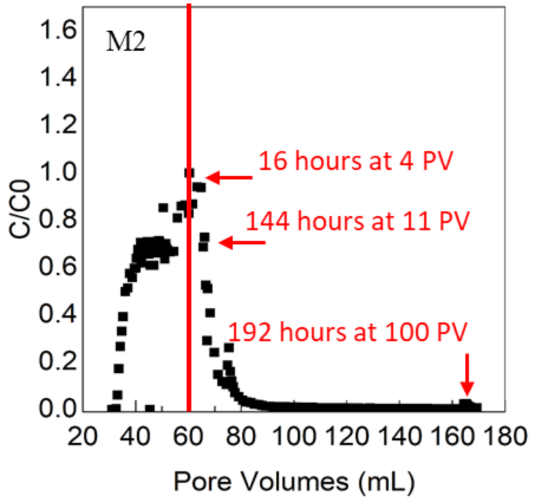


Column	*D* (cm^2min^{-1})	*R*
M1	0.055	0.958
M2	0.044	0.953

$$K_d = \frac{[contaminant_{sediment}]}{[contaminant_{solution}]}$$

Uranium Breakthrough Curves





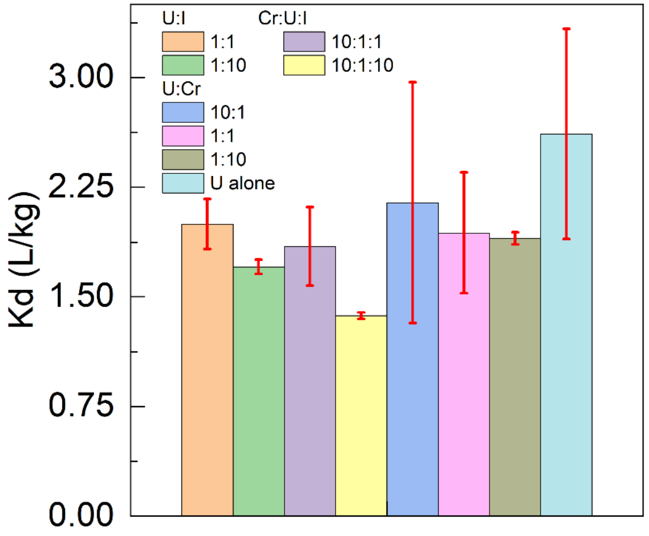
Column	K_d (L/kg)
M1	1.2
M2	1.5

Subtask 1.3: Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

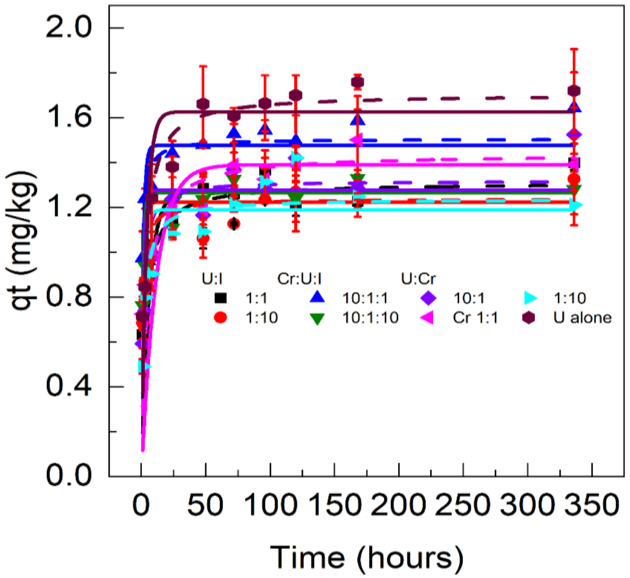
FIU Year 3 Research Highlights & Accomplishments:

Change in U K_d (10.5 µmol/L) in the presence of I-127 and Cr

$$K_d = \frac{[contaminant_{sediment}]}{[contaminant_{solution}]}$$



Change in U (10.5 µmol/L) kinetics pseudo-first (solid lines) and pseudo-second (dashed lines) in the presence of I-127 and Cr



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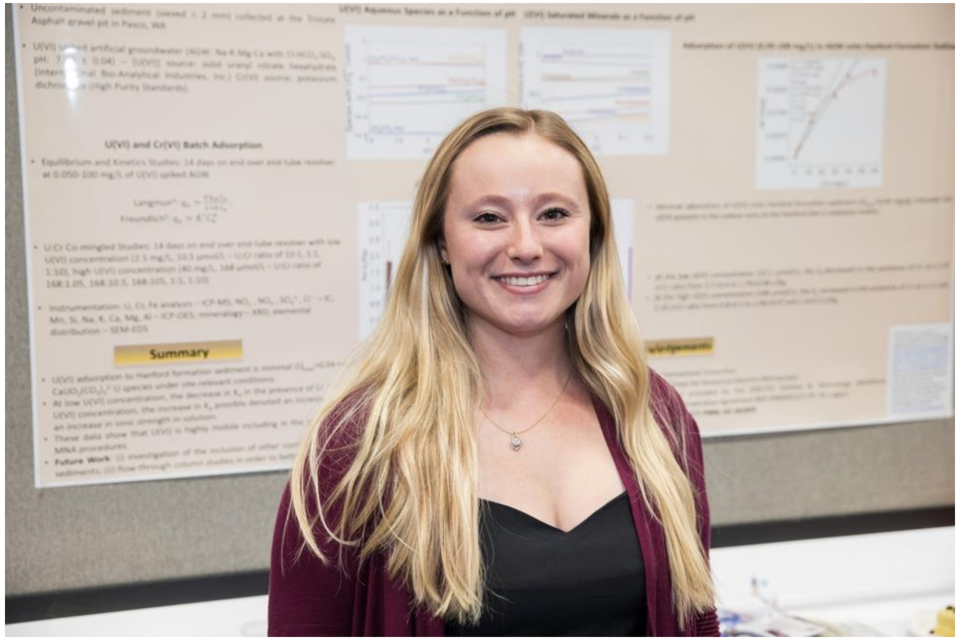
Subtask 1.3: Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

FIU Year 3 Research Highlights & Accomplishments:

- Waste Management Symposia 2023: Impact of Chromium (VI) as a Co-mingled Contaminant on the Adsorption of Uranium (VI) to Hanford Formation Sediment (poster)
- Accepted into the Department of Energy Office of Environmental Management Minority Serving Institutions Partnership Program Graduate Fellowship at PNNL
- Prepared a manuscript titled “Impact of Chromium (VI) as a Co-Contaminant on the Sorption and Co-Precipitation of Uranium (VI) in Sediments Under Mildly Alkaline Oxic Conditions” for journal submission



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Subtask 1.3: Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments

Summary

- Completion of U(VI) and U(VI) and Cr(VI) co-contaminant column experiments
- Completion of I-127, U(VI), and Cr(VI) co-contaminant batch experiments
- Prepared a manuscript titled Impact of Chromium (VI) as a Co-Contaminant on the Sorption and Co-Precipitation of Uranium (VI) in Sediments Under Mildly Alkaline Oxic Conditions for journal submission
- Poster presentation at Waste Management Symposia 2023: Impact of Chromium (VI) as a Co-mingled Contaminant on the Adsorption of Uranium (VI) to Hanford Formation Sediment

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Subtask 1.4: Experimental Support of Lysimeter Testing

Site Needs:

This task provides support to the large-scale field experiments at the Hanford Field Lysimeter Test Facility (FLTF) located in the 200-W Area of the Hanford site. The FLTF study is being initiated as a long-term experiment to provide data on glass and cementitious waste form durability, contaminant release from waste forms, and resulting transport in the near-field environment anticipated to be present at the Hanford Site Integrated Disposal Facility (IDF). The findings of the FLTF will be used to validate model predictions of long-term waste form behavior upon safe disposal of immobilized low-activity waste (ILAW) in the IDF and used in the IDF Performance Assessment (PA) calculations.

One of the planned configurations of the lysimeter units described in the Implementation Plan is to place grout waste forms above glass waste forms. This waste form arrangement has limited laboratory data regarding the dissolution of glass in the presence of grout-contacted water.

Objectives:

To investigate the impact of major elements, Ca and Si, present in the grout-contacted solution on the dissolution behavior of borosilicate glass at varying temperatures (25°C, 40°C, 70°C) using single-pass flow-through (SPFT) and static Product Consistency Test (PCT) (90°C).

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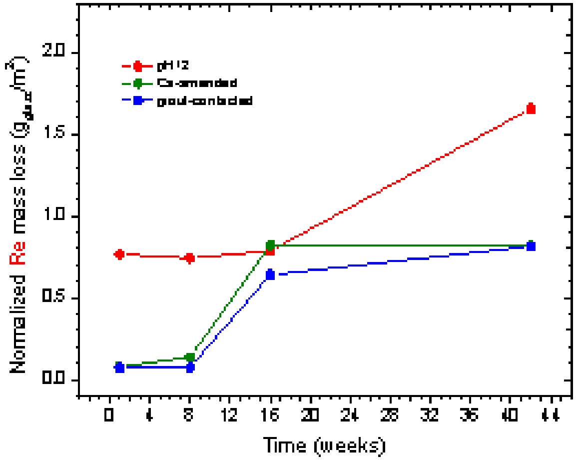
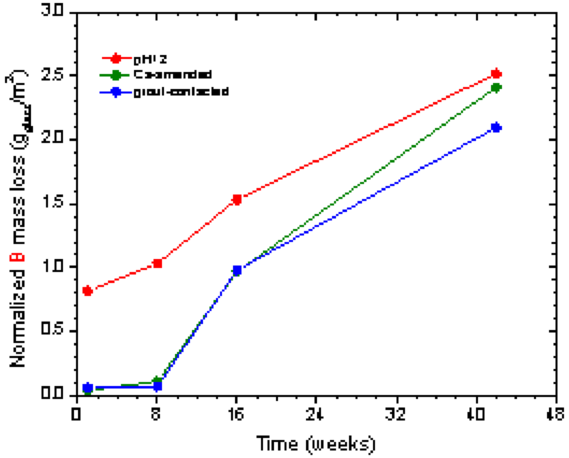
Subtask 1.4: Experimental Support of Lysimeter Testing

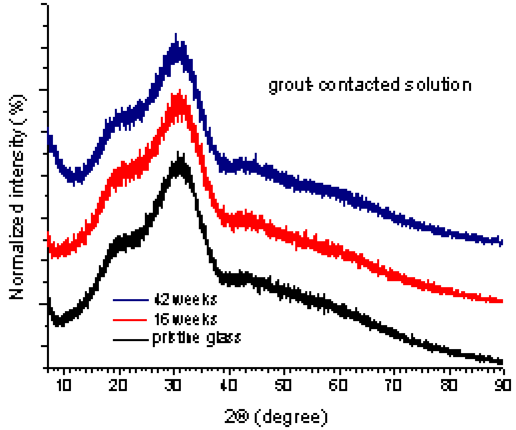
FIU Year 3 Research Highlights & Accomplishments:

- Investigated the impact of major elements on the dissolution behavior of borosilicate ORLEC28 glass.
  - Test matrix in PCT: long-term experiment at 90°C in pH 12 buffer, grout-contacted and Ca-amended solutions (8, 16 and 42 weeks).
  - Test matrix in PCT: triplicated reactors, Ca-amended solutions at pH 12 and 8.6 (0-130 mg/L Ca^{2+}).
- XRD and BET analyses of treated glass, SEM/EDS measurements in cross-sections of glass coupons to study glass erosion.
- Manuscript *"The corrosion behavior of borosilicate glass in the presence of cementitious waste forms"* ready for journal submission.

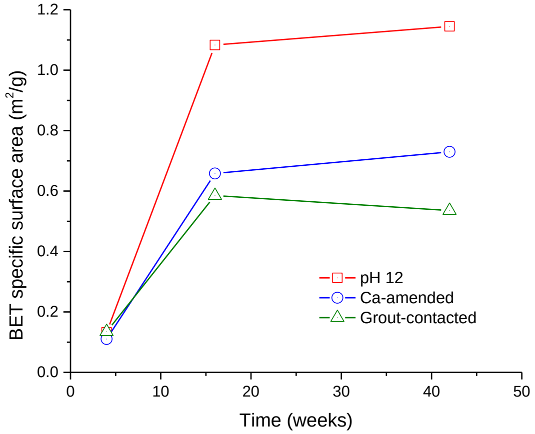




Normalized losses of Re and B by ORLEC28 glass in different solutions at 90°C in long-term PCT.



XRD patterns of glass treated in PCT for 42 weeks in grout-contacted solution.



BET surface area of glass treated in long-term PCT in different solutions vs. time.

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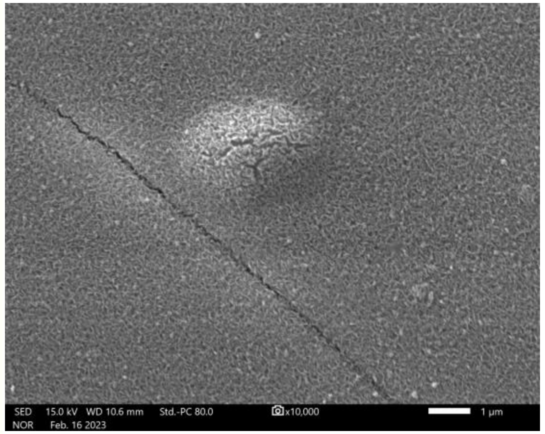
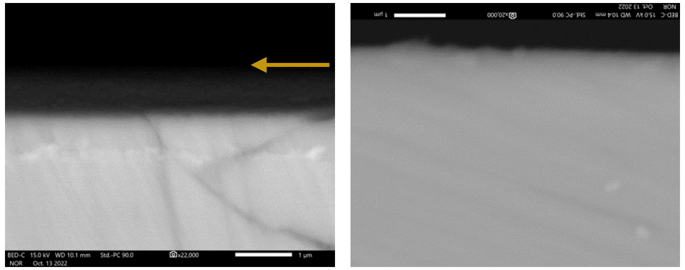
Subtask 1.4: Experimental Support of Lysimeter Testing

FIU Year 3 Research Highlights & Accomplishments:

Borosilicate glass dissolution behavior in different solutions (long-term PCT)



pH 12

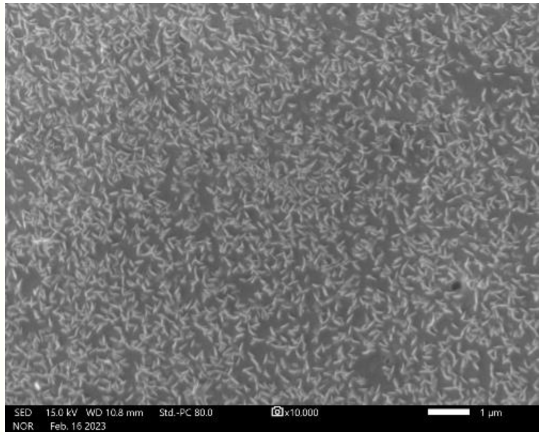


SEM images in cross-section of glass coupons treated for 4 weeks in the static PCT in pH 12 (left image) image) and Ca-amended (right image) solutions.

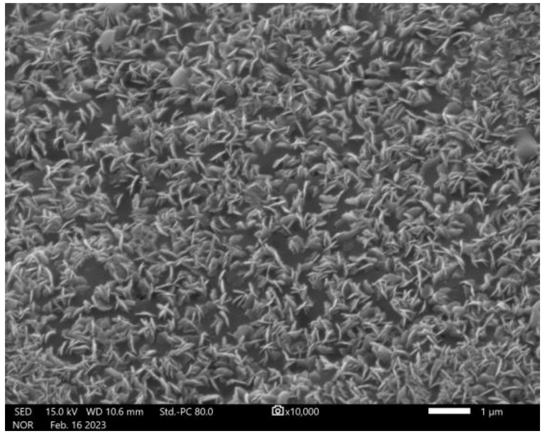
- Note: alternation layer ca. 500 µm in pH 12 treated glass coupon.

Composition of the glass particle surface measured by EDS. Measured area was clear from fines and precipitates. Surface of glass particle is depleted in Al and Si and enriched in Na that is in a good agreement with EDS study of glass coupons in cross-section.

	Pristine glass	pH 12 buffer	Ca-amended	Grout-contacted
Element	Atomic %	Atomic %	Atomic %	Atomic %
MgO	0.30(9)	0.46(6)	0.66(9)	0.26(11)
Al_2O_3	4.9(2)	5.7(8)	5.57(9)	5.0(1)
SiO_2	17.2(9)	19.8(3)	20.5(5)	18.7(2)
CaO	1.6(2)	1.6(4)	1.5(1)	2.22(9)
Fe_2O_3	0.27(2)	0.29(4)	0.24(1)	0.327(9)
Na_2O	14.4(15)	9.6(1.0)	7.4(1.2)	11.5(6)
K_2O	0.34(3)	0.38(2)	0.35(8)	0.56(18)
Zn	1.0(3)	1.1(1)	1.13(6)	1.34(12)
ZrO_2	1.8(8)	2.03(7)	2.13(8)	1.80(2)
TiO_2	0.2(1)	0.31(2)	0.3(1)	0.34(4)



Grout-contacted



Ca-amended

SEM images of glass surface after 42 weeks of PCT at 90^{o}C.

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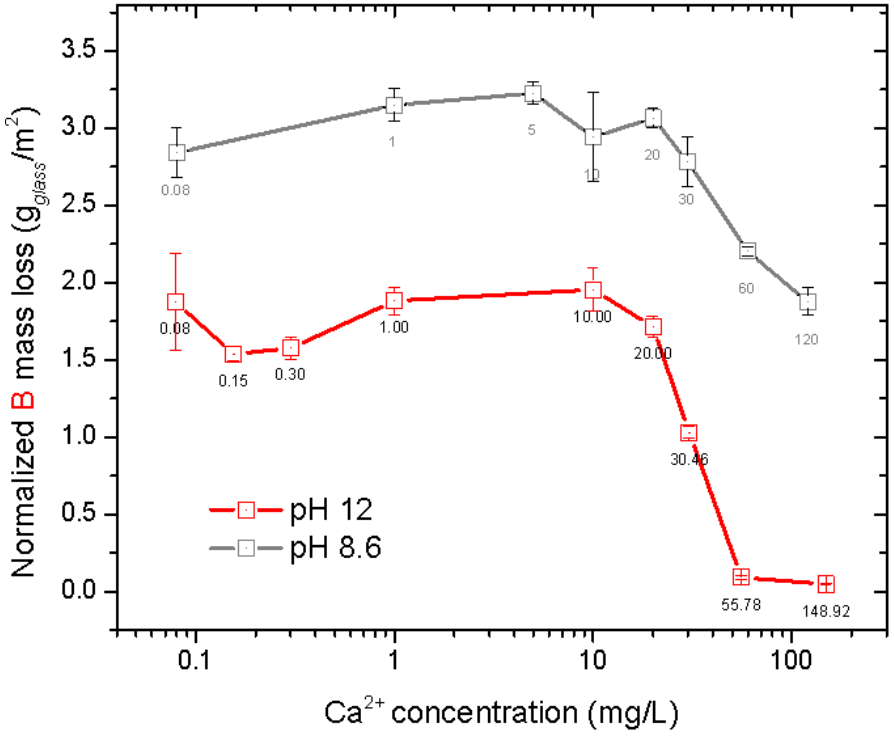
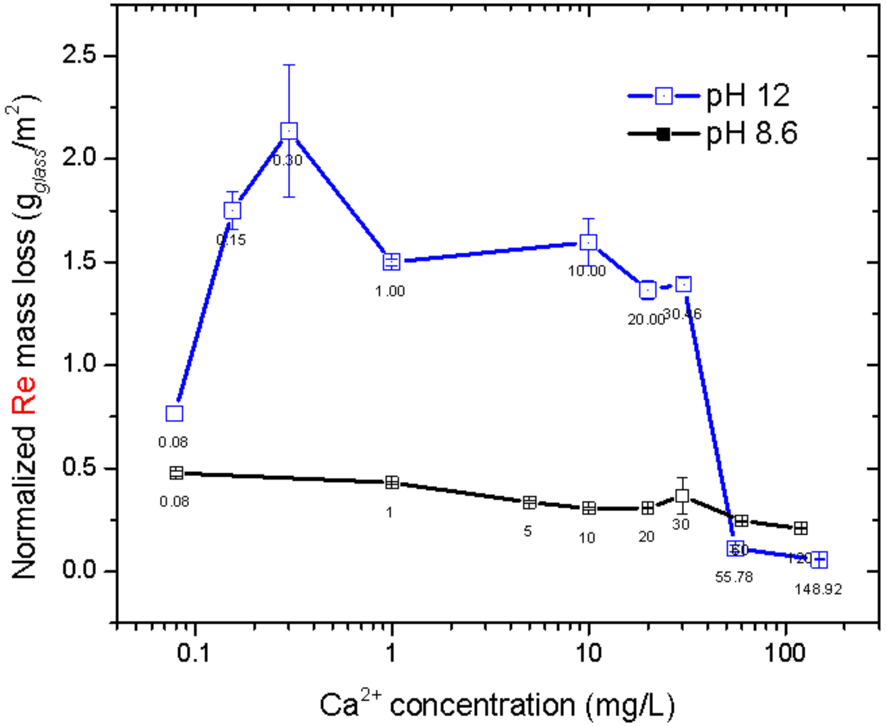
FIU Year 3 Research Highlights & Accomplishments:

PCT with Ca-amended solution at different pH: Normalized release rates for Re, B





- Ca^{2+} inhibits glass dissolution at concentration above 20 mg/L (pH 12 and 8.6).
- Boron dissolution rate increases with pH decrease.
  - Unexpected result which needs confirmation and further study.
  - PCTs with Ca-amended solutions with intermediate pH 10 are in progress.

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Subtask 1.4: Experimental Support of Lysimeter Testing

FIU Year 4 Projected Scope

- Investigate glass dissolution in contact with Al- and grout/sediment-contacted groundwater to investigate any common ion effect.
  - Al concentrations in the leachate will range from 0.3 ppm to 30 ppm at different pHs (7, 9, 10, 11).
- Support glass characterization studies via microscopy, spectroscopy, and X-ray diffraction techniques.

Major elements present in grout-, sediment-, and grout/sediment-contacted solutions are identified through analysis.

- **The impact of two major elements, Si and Ca, on glass dissolution has been systematically investigated.**

Element	Concentrations, μg/L		
	Grout-contacted	Sediment-contacted	Grout/sediment-contacted
pH	11.52	8.68	8.30
B	172(6)	2.8(6)	112.1(9)
Re	0.052(4)	0.006(3)	0.08(9)
Si	**6397(83)**	**22711(443)**	**22719(199)**
Al	**423(118)**	**391(24)**	**18(5)**
Ca	**111506(2312)**	**2934(45)**	**48634(449)**
Mg	33(2)	106(5)	**24821(259)**
K	3064(226)	6037(347)	18947(1084)
Fe	0	291(66)	0

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Subtask 1.5: Remediation Research on Combination of Reduction and Sequestration Treatment (NEW)

Site Needs:

Subtask evaluates potential *in situ* treatment technologies for the vadose zone, groundwater, and perched water zone in the 200 Area at Hanford. One limitation of strong reductants technology is U(VI) and Tc(VII) reoxidation and remobilization in the aqueous phase when conditions turn aerobic. To counter this, strong reductants can be coupled with other remediation tech for prolonged sequestration potential. Batch experiment results will inform Tc remobilization behavior in co-contaminant presence and guide remedial actions.

Objectives:

Objective #1: Assess the immobilization of Tc(VII) by employing a combined treatment approach involving strong reductants identified in subtask 1.2, followed by ammonia gas injection, in Hanford sediments spiked with Tc(VII) (excluding co-contaminants). Explore the possibility of remobilization under specific site conditions.

Objective #2: Quantify the immobilization of Tc(VII) using a combined treatment of Tc(VII) by strong reductants in the presence of co-contaminants, U(VI), nitrate, and others targeting contaminants of concern followed by ammonia gas injection and investigate potential remobilization of Tc(VII) or other targeted contaminants throughout the process.

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Subtask 1.5: Remediation Research on Combination of Reduction and Sequestration Treatment (NEW)

FIU Year 3 Research Highlights & Accomplishments:

- In a process of a developing a test plan, ordering necessary laboratory supplies for the experiments including a gas cylinder with 5% ammonia gas in 95% nitrogen as well as ammonia and sodium hydroxide.
- Preparing to conduct preliminary experiments to examine sequestration of redox sensitive contaminants via sequentially applied ZVI followed by ammonia gas treatment.
- Seeking an enthusiastic PhD student interested in pursuing this innovative research opportunity.

FIU

Applied Research Center

Subtask 1.5: Remediation Research on Combination of Reduction and Sequestration Treatment (NEW)

FIU Year 4 Projected Scope

- Develop a test plan;
- Initiate experiments using sediments spiked with Tc(VII) only and Tc(VII) with co-contaminants such as U(VI) and nitrate.
  - This would allow the reduction of redox sensitive contaminants under site specific pH conditions followed by the application of ammonia gas to maximize contaminant sequestration by coating of aluminosilicates on top of reduced U and Tc phases (Szecsody et al., 2012; Szecsody et al., 2010).

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Task 2

Remediation Research and Technical Support for the Savannah River Site

Applied Research Center

Subtask 2.1: Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site

Site Needs:

- **Iodine-129** poses a substantial clean-up problem at Savannah River Site due to its perceived high mobility in the environment, toxicity, and long half-life (~16 million years), as well as it having one of the lowest maximum contamination levels (1 pCi L^{-1}) of all radionuclides.
- Wetlands at the F-Area have been an important sink for I-129 and other contaminants. The complex and diverse physical and biogeochemical processes within the wetlands are mainly responsible for retaining these contaminants.
- However, these areas are sensitive to changing boundaries and geochemical conditions, resulting in the release of iodine-129 into surrounding areas.

Objectives:

- The sorption study of iodine on the wetland soils will improve understanding of the factors that contribute to the attenuation of iodine-129 at the F-Area wetlands and will provide SRS and the DOE with the ability to remediate I-129 from the F-Area more effectively.
- The removal study of iodine is to evaluate the efficacy in the use of amendments such as PM-199 and MRM that can be deployed in the subsurface to enhance the attenuation of I-129 and identify the optimal conditions for the amendment efficacy.

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FIU Year 3 Research Highlights & Accomplishments:

- Investigated the attenuation of iodide and iodate by wetland soils at various depths under different environmental conditions, such as temperature and redox potential
  - Solid to liquid ratio: 25 g/L
  - Concentration: 100 ppb
  - Depth intervals: 1-3 ft, 5-6 ft, and 13-14 ft
  - pH : 5.5
  - Temperature: 22°C and 8°C
  - Aerobic vs Anaerobic

Soil parameters at three different depth intervals

Soil depth interval (m)	pH	Total Organic Carbon (mg/kg)	Aluminum (mg/kg)	Iron (mg/kg)	Manganese (mg/kg)	Sulfur (mg/kg)
0.3 – 0.9	4.79±0.10	25,300–119,000	5,310 – 7,130	1340 – 8940	20.3 – 126	170–297
1.5 – 1.8	5.05	41,700	4,310	215	3.49	356
4.0 – 4.3	5.49	350	2,920	180	4.21	27

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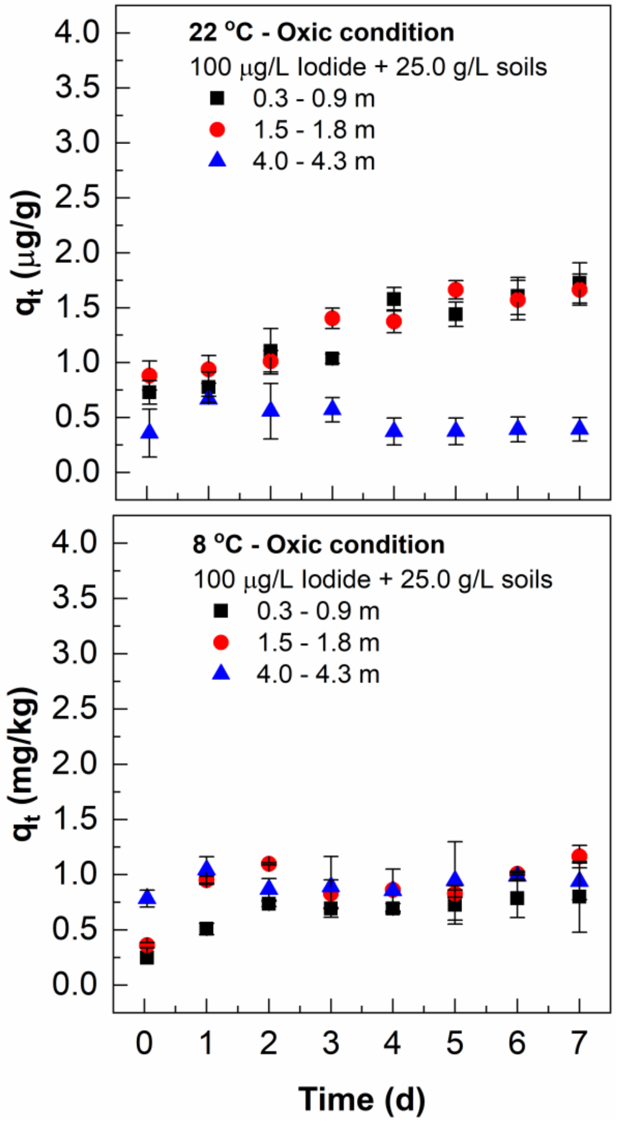
Subtask 2.1: Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site

FIU Year 3 Research Highlights & Accomplishments:

- At 22°C, an apparent instantaneous uptake of iodide from solution occurred for all soil layers in less than 1 h, followed by a time-dependent sorption.
  - The sorption of iodide onto the surface of 0.3 - 0.9 and 1.5 - 1.8 m soil samples gradually increased (qt,7d = 1.726 ± 0.183 and 1.665 ± 0.142 mg/kg, respectively).
  - Sorption onto 4.0 - 4.3 m sample was stabilized over the next 7 days because of the low amount of organic matter.
- At 8°C, iodide initially adsorbed onto all soil samples within 24 hours and the sorption was slower and stabilized over the next 7 days.

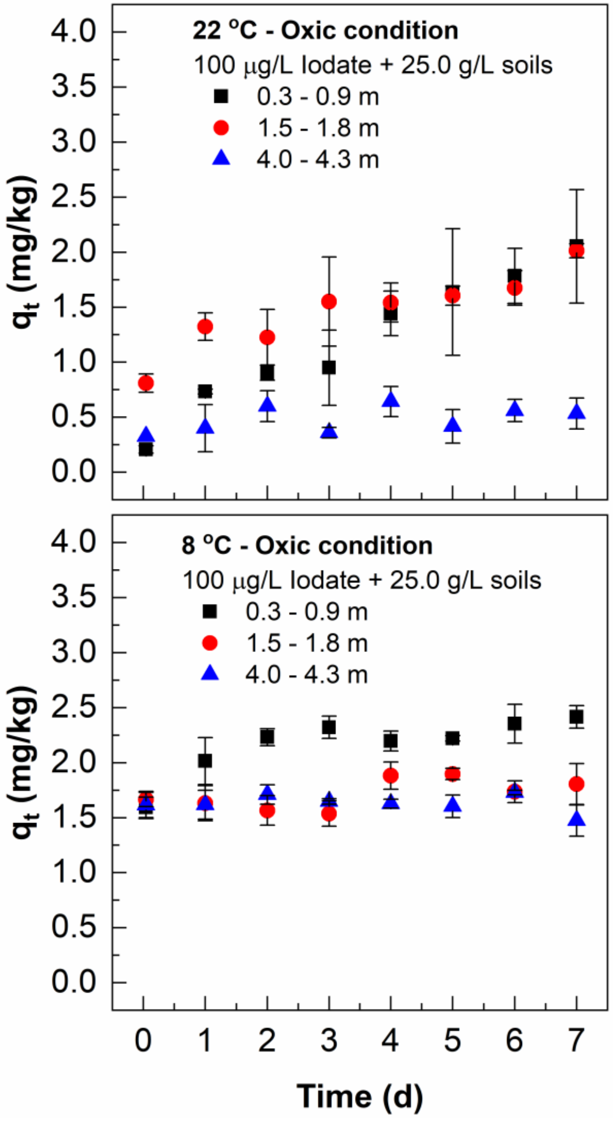


Applied Research Center

Subtask 2.1: Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site

FIU Year 3 Research Highlights & Accomplishments:

- Uptake of iodate by the soil at different depths also followed a similar quasi-steady-state pattern with rapid initial loss of iodate and rapid immobilization by reduction at reactive sites in organic matter.
- In the subsoil layer (4.0 - 4.3 m), iodate uptake was higher than that of iodide at room temperature (qt,7d = 0.533 ± 0.140 and 0.392 ± 0.107 mg/kg for iodate and iodide sorption at 22°C, respectively).
- The largest initial iodate uptake was observed in all soils at 8°C.
- Iodate more readily adsorbs onto the positively charged metal-oxide surface and nitrogen-containing constituents of soil organic matter as the initial sorption of IO_3^- was slightly faster than that of I^-.



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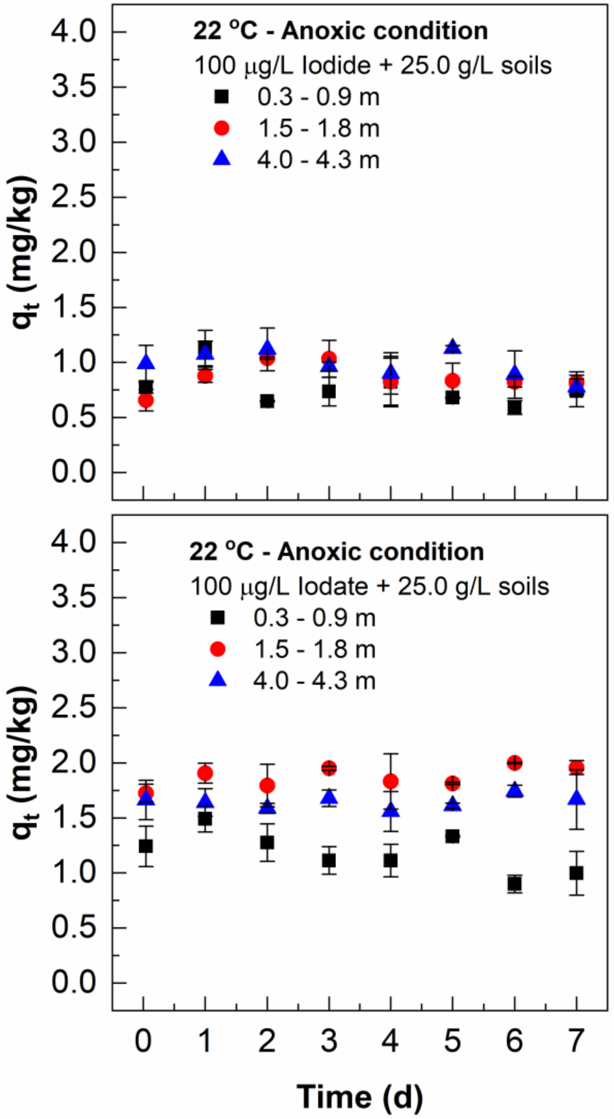
Subtask 2.1: Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site

FIU Year 3 Research Highlights & Accomplishments:

- The q_t values of I^- uptake top and intermediate layers soil samples in anoxic conditions were significantly less than those completed under oxic conditions.
  - qt = 0.740 ± 0.143, 0.817 ± 0.097

- The reduced sorption of iodine onto organic-rich soils under an anoxic environment may be linked to both the microbial activity and the chemical reactions involving I^-.



Subtask 2.1: Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site

- Presented posters at annual DOE Fellows poster exhibition and at Waste Management 2023.
- DOE Fellow Phuong Pham successfully defended her research and graduated with a Ph.D. in chemistry in Spring 2023.
- Joined SRNL as Postdoctoral Scholar via MSIPP program.

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FIU Year 4 Projected Scope

- Continue to investigate the attenuation and release of iodine in the wetland sediments and the use of amendments such as organoclays (MRM, PM-199) to mitigate the release of iodine from wetland soils.
- Conduct experiments to understand the effect of:
  - Redox Conditions: perform experiments in anoxic conditions
  - pH on desorption: pH = 4 - 8
  - Competition of ions: nitrate and other relevant ions

FIU Applied Research Center

Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on Contaminant Removal

Site Needs:

- Low-cost unrefined humic substances are potential amendments for treatment of uranium in groundwater associated with the F-Area Seepage Basin plume.
- These experiments will determine necessary parameters helping to simulate the creation of a sorbed humate treatment zone in the acidic groundwater contaminated with uranium.

Objectives:

- Investigate, via batch experiments, the sorption behavior of modified humic substances (KW-30) for groundwater remediation and the effect of sorbed humic substances on co-contaminant (uranium, strontium and Iodine) removal.

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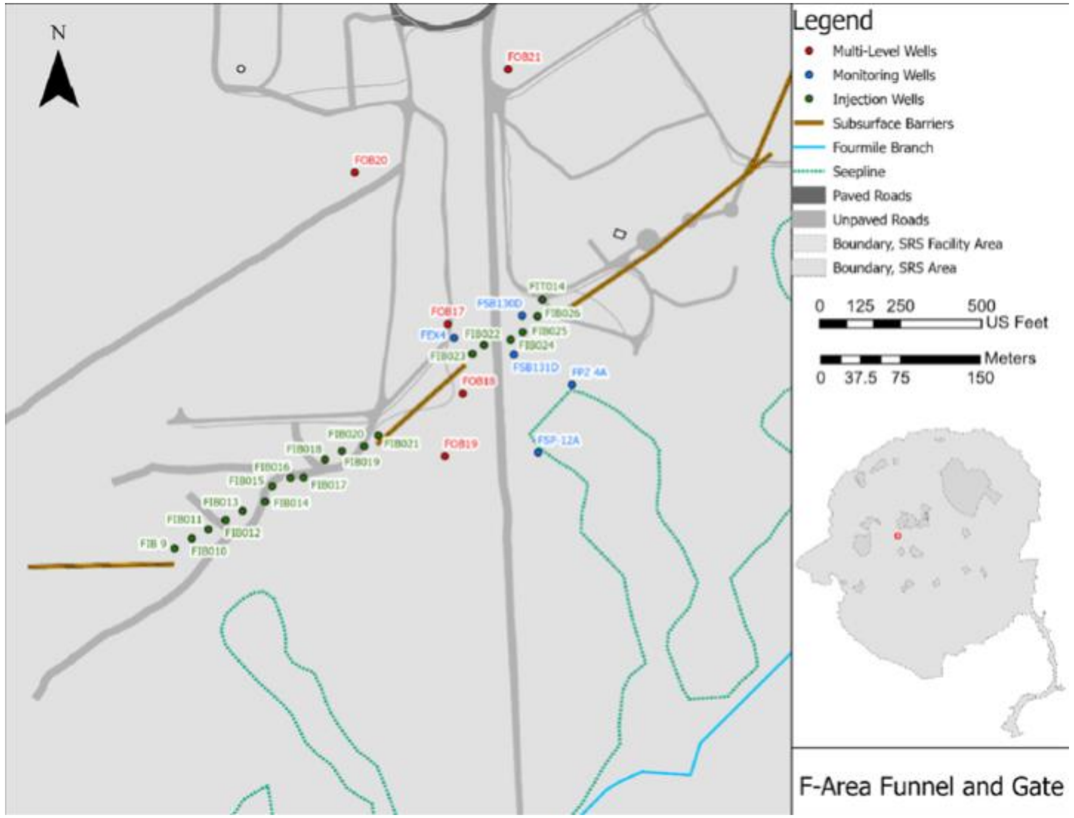
Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on the Contaminant Removal

FIU Year 3 Research Highlights & Accomplishments:

- Formulated synthetic groundwater (SGW) recipe
  - ➢ Used data FOB 21 and FOB20 wells from SRS F-Area (wells close to basins to represent untreated area)
- Elements of interest
  - ➢ Calcium
  - ➢ Sodium
  - ➢ Magnesium
  - ➢ Potassium
  - ➢ Sulfate
  - ➢ Nitrate
  - ➢ Chloride



	g/mol	K+	SO42-	Mg2+	Ca2+	Cl-	NO3-	Na+
CaCl2	110.98				0.041	0.082		
NaSO4	142.04		0.133					0.133
MgCl2	95.211			0.077		0.155		
NaCl	58.44					0.313		0.313
KCl	74.55	0.025				0.025		
NaNO3	84.99						1.845	1.845
TOTAL		0.025	0.133	0.077	0.041	0.574	1.845	2.290

FIU Applied Research Center

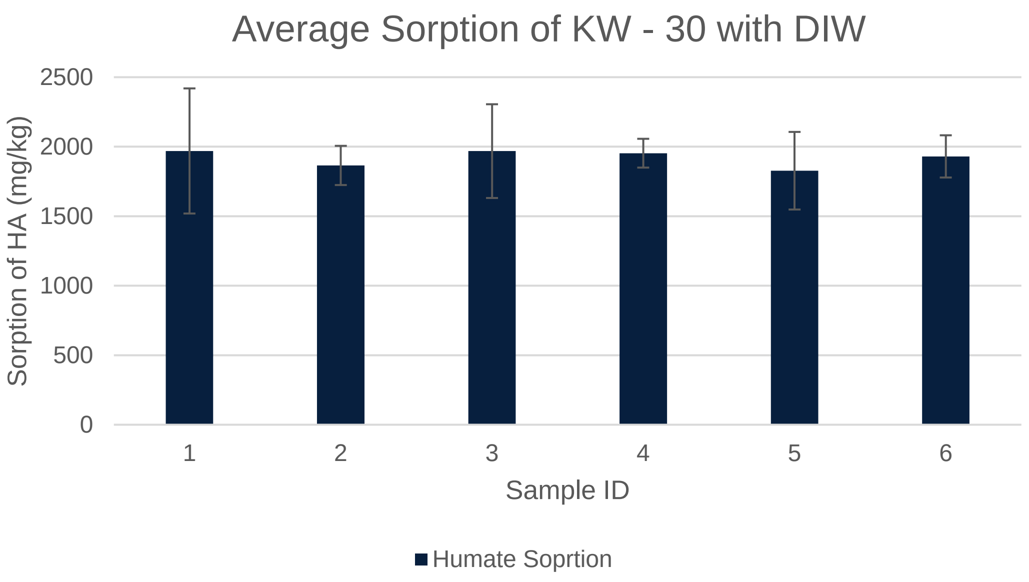
Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on the Contaminant Removal

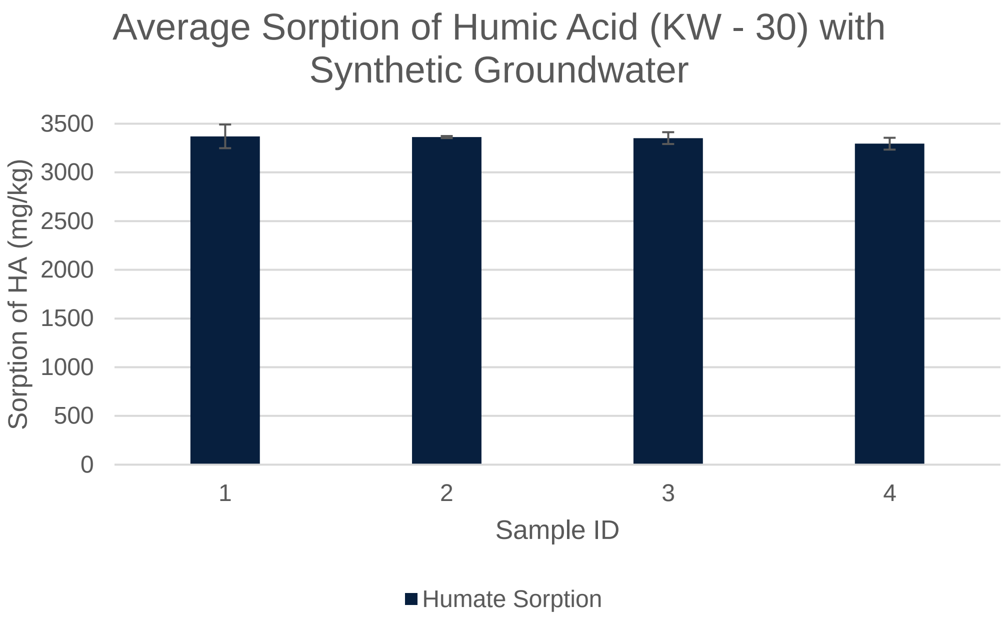
FIU Year 3 Research Highlights & Accomplishments:

- Studied the influence of humate and GW ions on kinetics of uranium removal
  - 200 mg of SRS sediment*
  - pH - 4 (0.1m HCl/NaOH)
  - Uranium: 700 ppb
  - Collected 200 µl aliquots for 2 weeks
  - Analyzed samples via ICP-MS

- **Control Samples** - no sediment
- **Uncoated Sediment Samples** - 200mg of sediment with no KW-30
- **Coated Sediment** - 200mg of sediment coated with KW-30

Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on the Contaminant Removal





Average sorption of humic acid with deionized water ~2000 mg/kg (left) and with synthetic groundwater ~3300 mg/kg (right).

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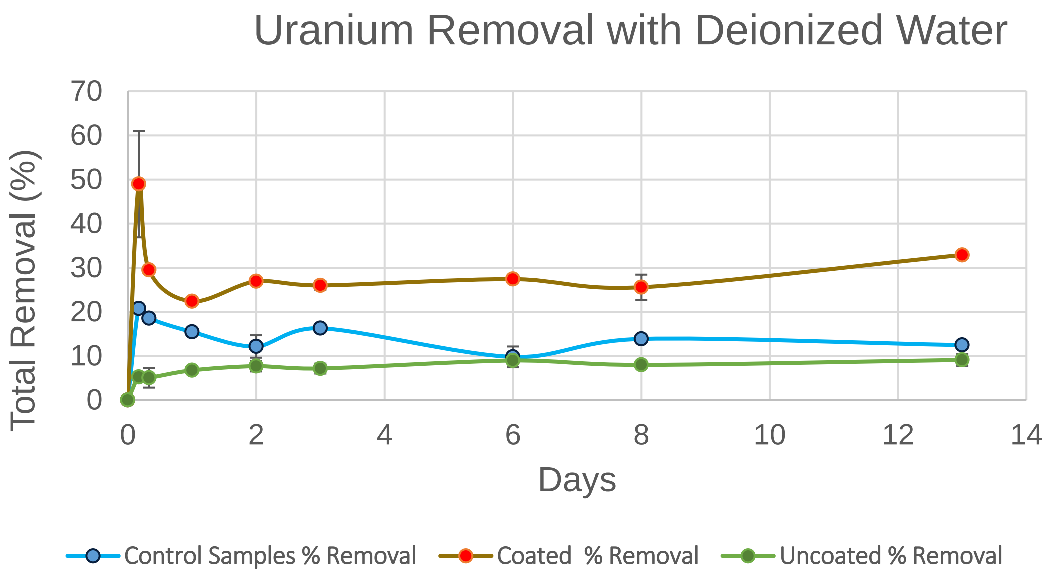
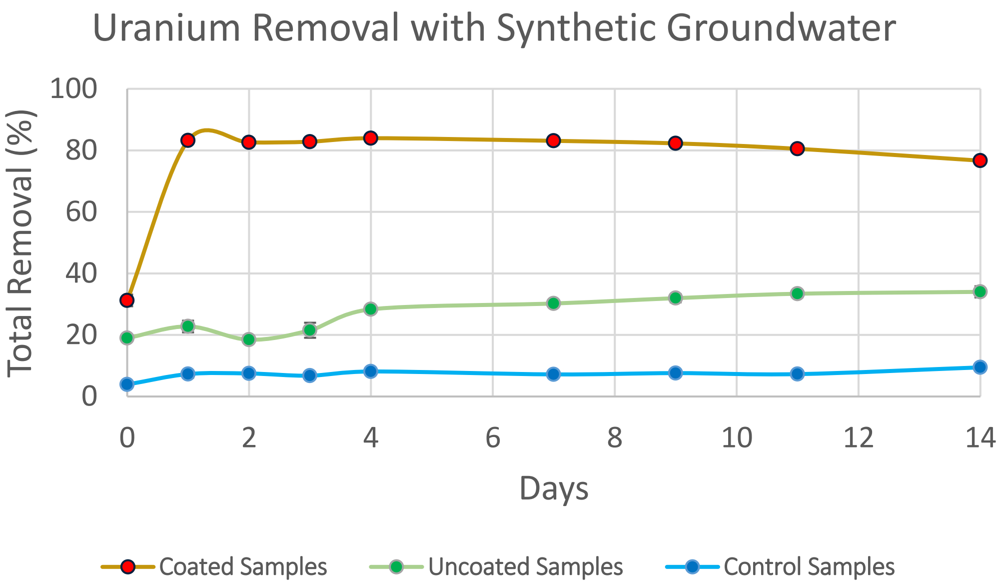
Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on the Contaminant Removal





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Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on the Contaminant Removal

FIU Year 4 Projected Scope

- Perform experiments with other contaminants and comingled contaminants
  - Effect pf pH
  - Effect of ORP
  - Effect of initial concentration (isotherms)
  - Desorption

FIU Applied Research Center

Task 3

Contaminant Fate and Transport Modeling for the Savannah River Site

Applied Research Center

Task 3: Contaminant Fate and Transport Modeling for the Savannah River Site

Overall Problem:

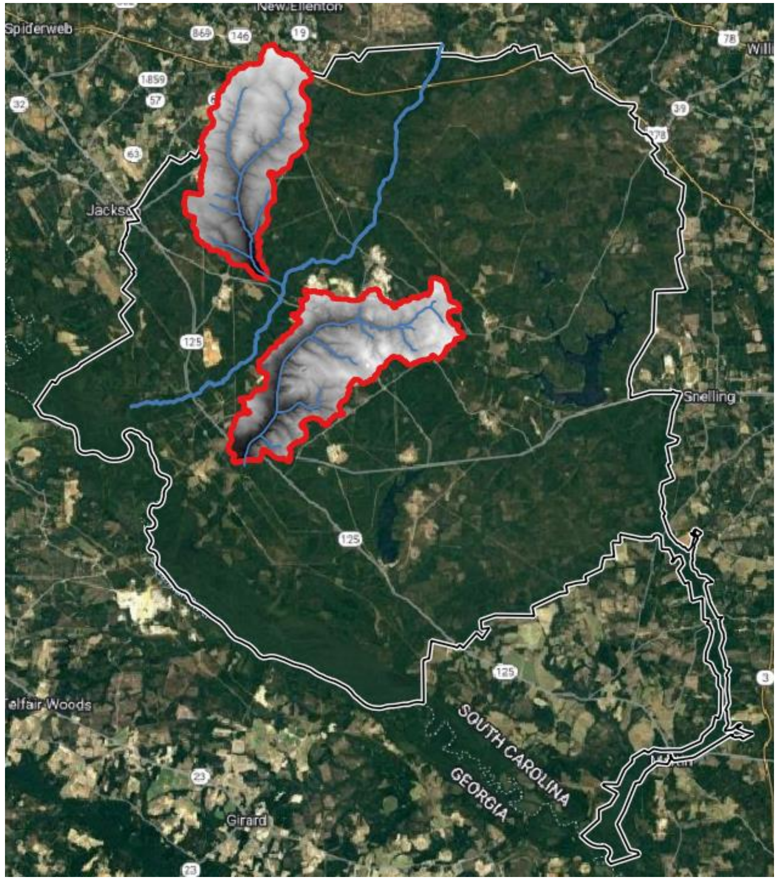
- SRS & other DOE sites challenged with heavy metal & radionuclide surface & subsurface contamination.

Site Needs:

- Numerical models to study impacts of hydrological extremes (i.e., heavy precipitation, floods, drought) due to climate change on contaminant transport in SRS stream systems.
- Evaluation applied remediation technologies.
- Establishment of long-term monitoring strategy.

Objectives:

- Use Tims Branch as braided stream system test bed for model dev.
- Duplicate process for critically contaminated SRS watersheds e.g., Fourmile Branch.
- Use models to evaluate impact of extreme hydrological events & long-term hydrological changes on GW-SW interactions, and fate & transport of major contaminants of concern in SRS streams.
- Collect field data to support model calibration & validation.
- Train FIU grad. & undergrad. students (DOE Fellows).



Tims Branch & Fourmile Branch watersheds at SRS.

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Subtask 3.1: Calibration of the Tims Branch Watershed Model and Scenario Analysis

FIU Year 3 Research Highlights & Accomplishments:

Tims Branch Hydrology Modeling

- Issue with long-term stability of MIKE SHE/MIKE 11 hydrology model (at 50m res.) of Tims Branch watershed & representativeness of model parameters for long-term simulations.
  (Model provides good results for short timescales)

Objective for FIU Year 3:

- Finalize model setup and define hydrological parameters for long-term model simulations.

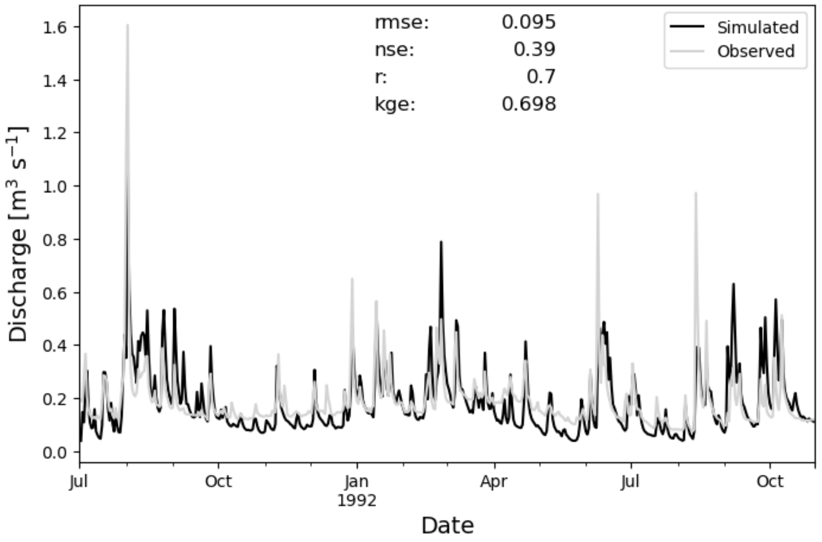
Approach:

- Use existing 50m res. model.
- Update selected model parameters.
- Develop procedure for long-term simulations.

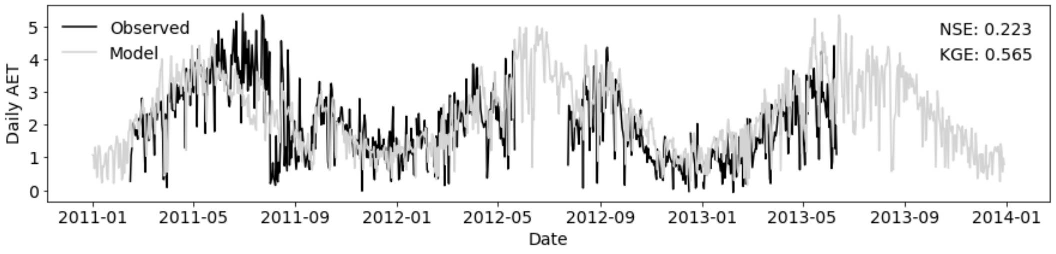
Results:

- Completed optimization/calibration of Tims Branch (MIKE) **hydrological** model for long-term simulations (Milestone 2022-P2-M10).

Results show model can simulate runoff, evapotranspiration, channel infiltration and exfiltration.



MIKE SHE/MIKE 11 sim. vs. obs. discharge at USGS station 02197309 for Jul. 1991 – Oct. 1992.
(rmse = root mean squared error; nse = Nash-Sutcliffe model efficiency, r = correlation, and kge = Kling-Gupta Efficiency)



Obs. daily evapotranspiration from nearby flux tower vs. MIKE SHE simulated actual evaporation for forest land cover class for 2011-2013.
(NSE) of 0.223, (KGE) of 0.565

Subtask 3.1: Calibration of the Tims Branch Watershed Model and Scenario Analysis

FIU Year 3 Research Highlights & Accomplishments:

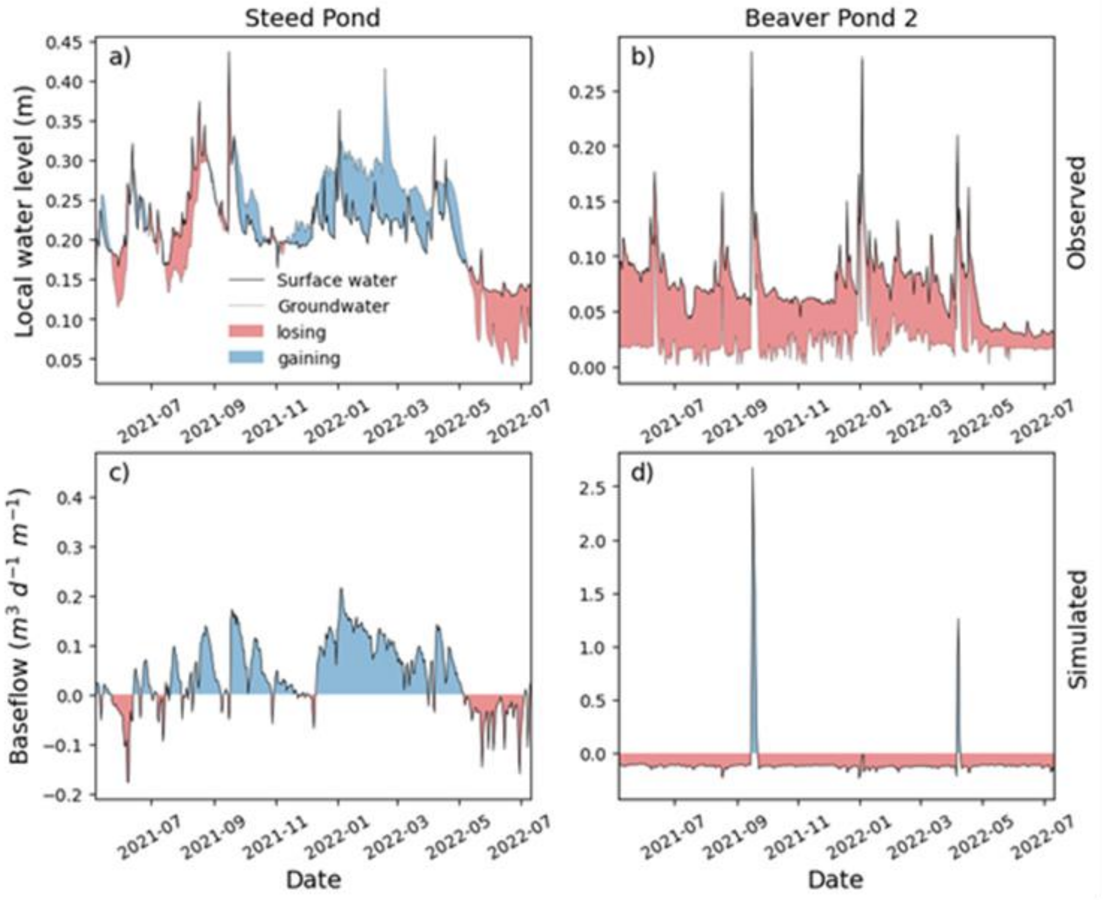
Tims Branch Hydrological Modeling

Implementation

- Model runtime too slow to allow for extensive calibration.
- Updated model parameters to improve the runoff response in channel network during both winter (high flow) and summer (low flow) conditions (i.e., focus locations of interest).
- Perform multi-year simulations of max 2-5 years, which reduces overestimation of baseflow at longer timescale. Merge period to obtain longer simulation series.

Conclusions

- Model provides good simulations of both runoff and evapotranspiration at the catchment scale.
- Model simulates infiltration/exfiltration variability in line with observations.
- Model provides detailed information on interaction between braided (ponds) and incised sections of the channel network and how this impacts flow velocity variations.



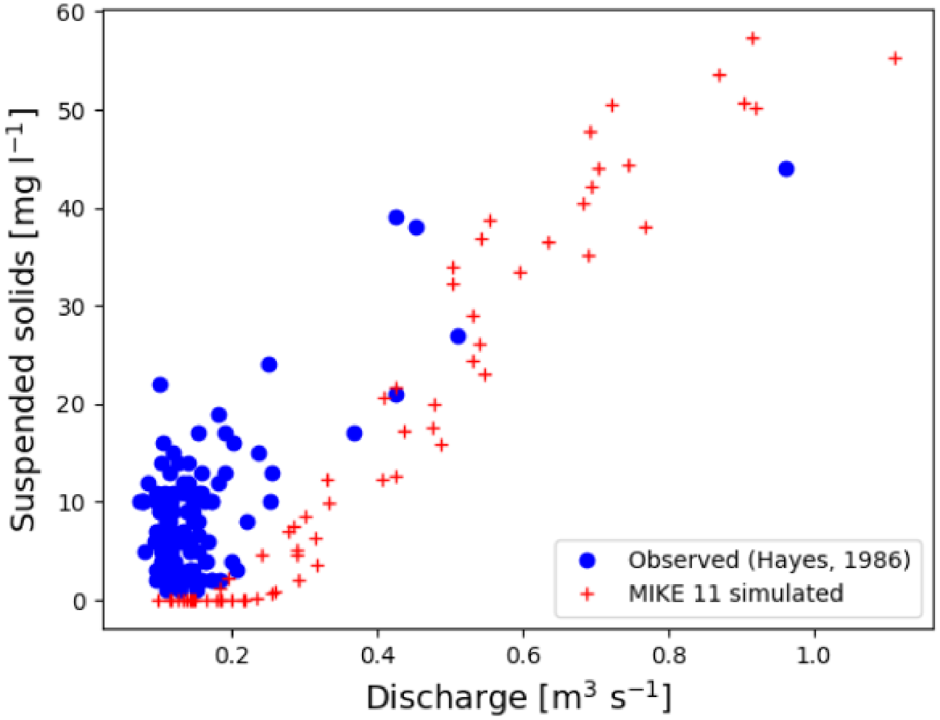
Upper row: Piezometer observations of local SW (solid) and surrounding GW level (dashed). Lower row: Simulated baseflow into river network, for Steed Pond (a) and Beaver Pond (d) locations. *Red color – river infiltration (losing) conditions; blue color – exfiltration (gaining) conditions.*

Subtask 3.1: Calibration of the Tims Branch Watershed Model and Scenario Analysis

FIU Year 3 Research Highlights & Accomplishments:

Tims Branch Event-Based Simulations of Sediment Transport

- Calibrated suspended sediment transport model.
- Focus on the impact of **individual storm events**, for return period simulations for suspended solids:
  - 5, 10, 25, 100, 500-year return periods for 24-hr storm events
- Awaiting updated version of MIKE ECO Lab to enable uranium transport simulations
- *Delayed Milestone 2022-P2-M11: Complete simulations and evaluation of event-based uranium transport model for Tims Branch (Subtask 3.1), due 7/14/2023*.



Calibrated performance of simulated sediment transport

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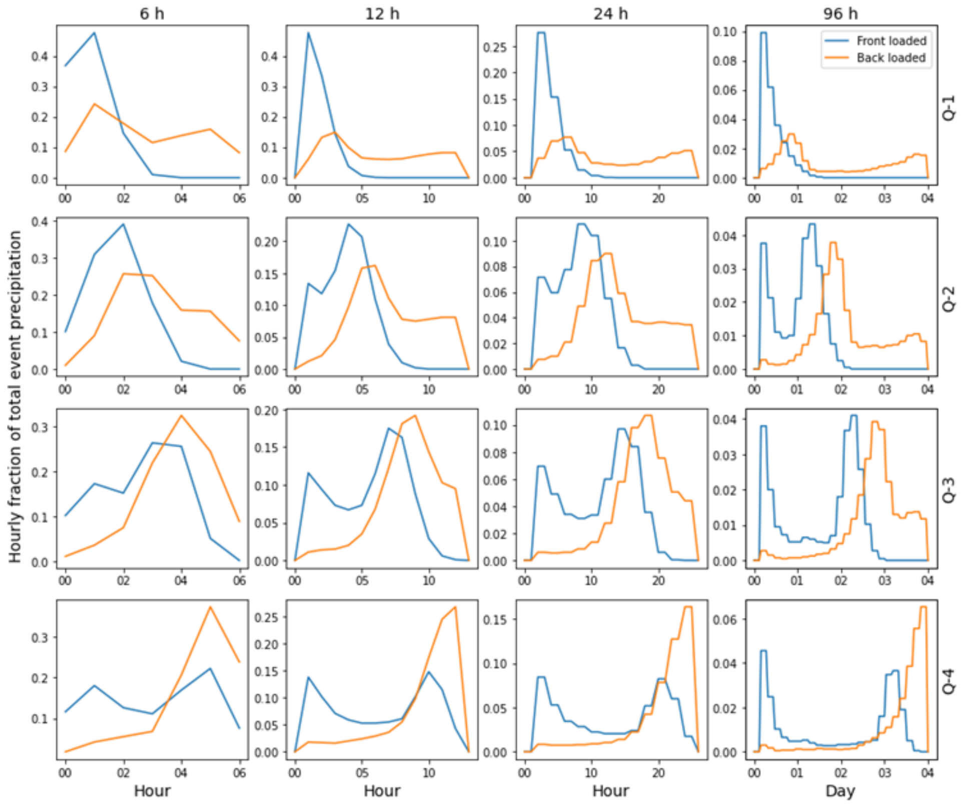
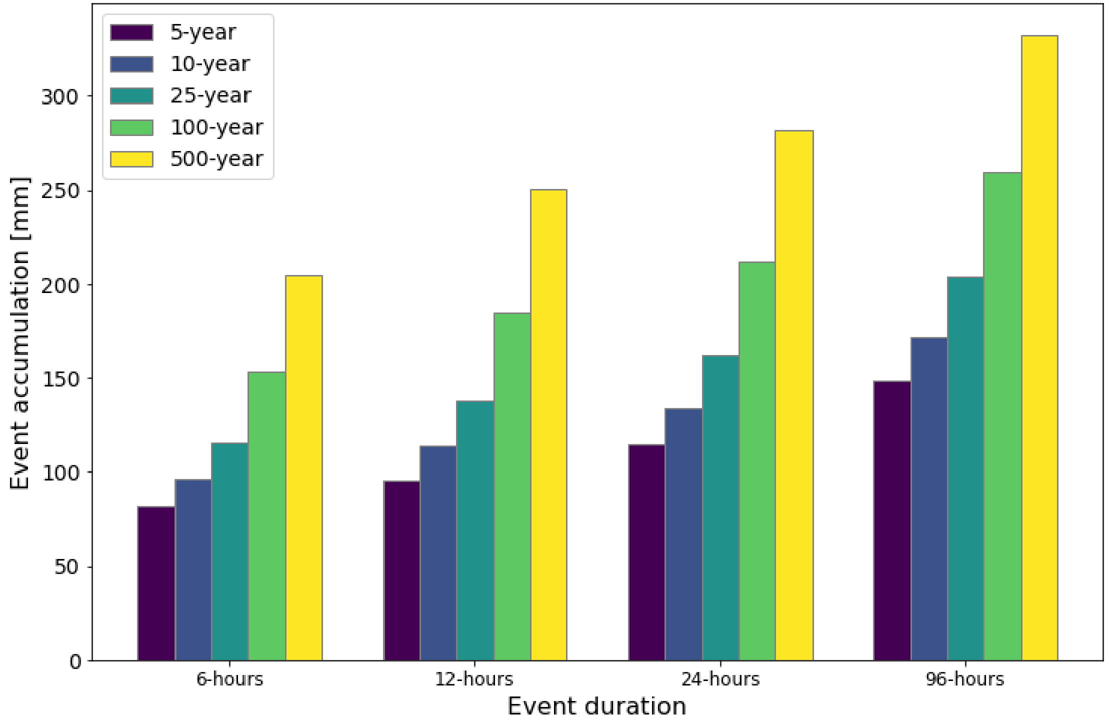
Subtask 3.1: Calibration of the Tims Branch Watershed Model and Scenario Analysis

FIU Year 3 Research Highlights & Accomplishments:

Tims Branch Event-Based Simulations of Sediment Transport





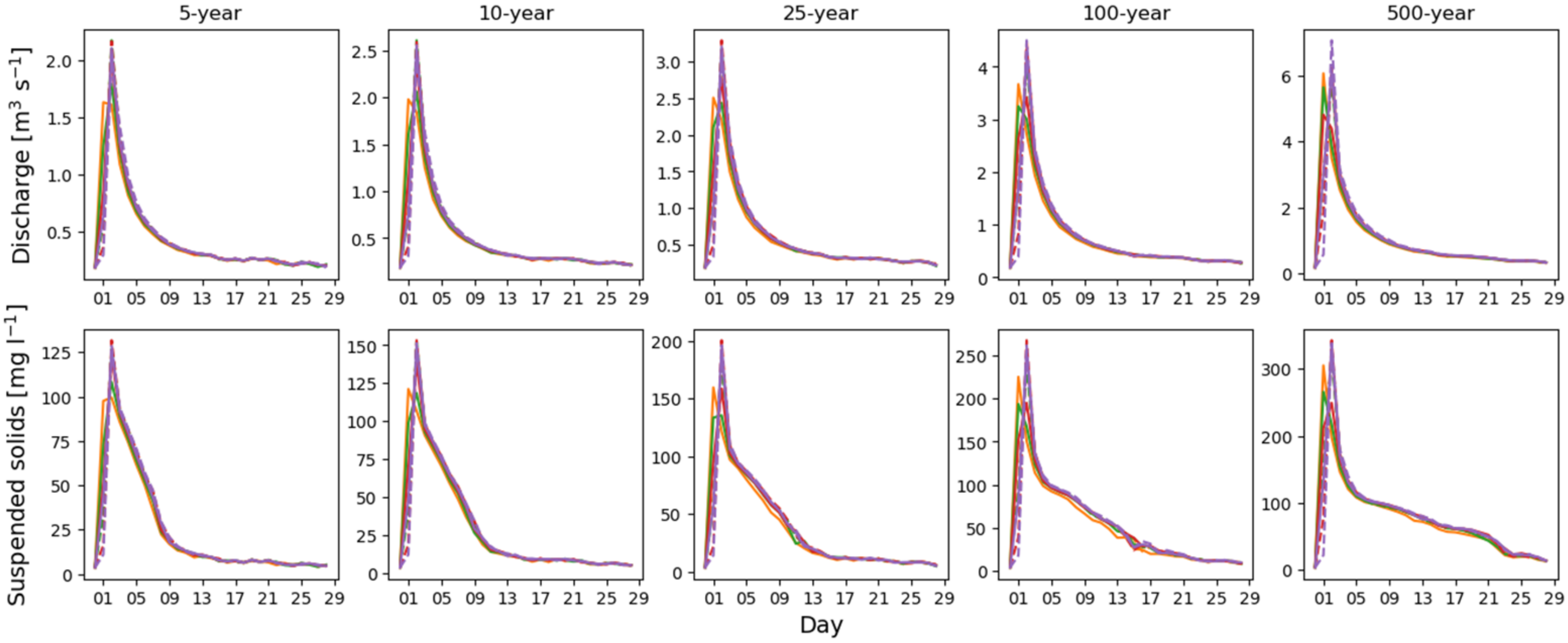
- Results above focused on 24-hour simulations.
- Model run from January 1 until March 5.
- 24-hour event is forced on January 31, with rest of the period used for recession.

Subtask 3.1: Calibration of the Tims Branch Watershed Model and Scenario Analysis

FIU Applied Research Center

FIU Year 3 Research Highlights & Accomplishments:

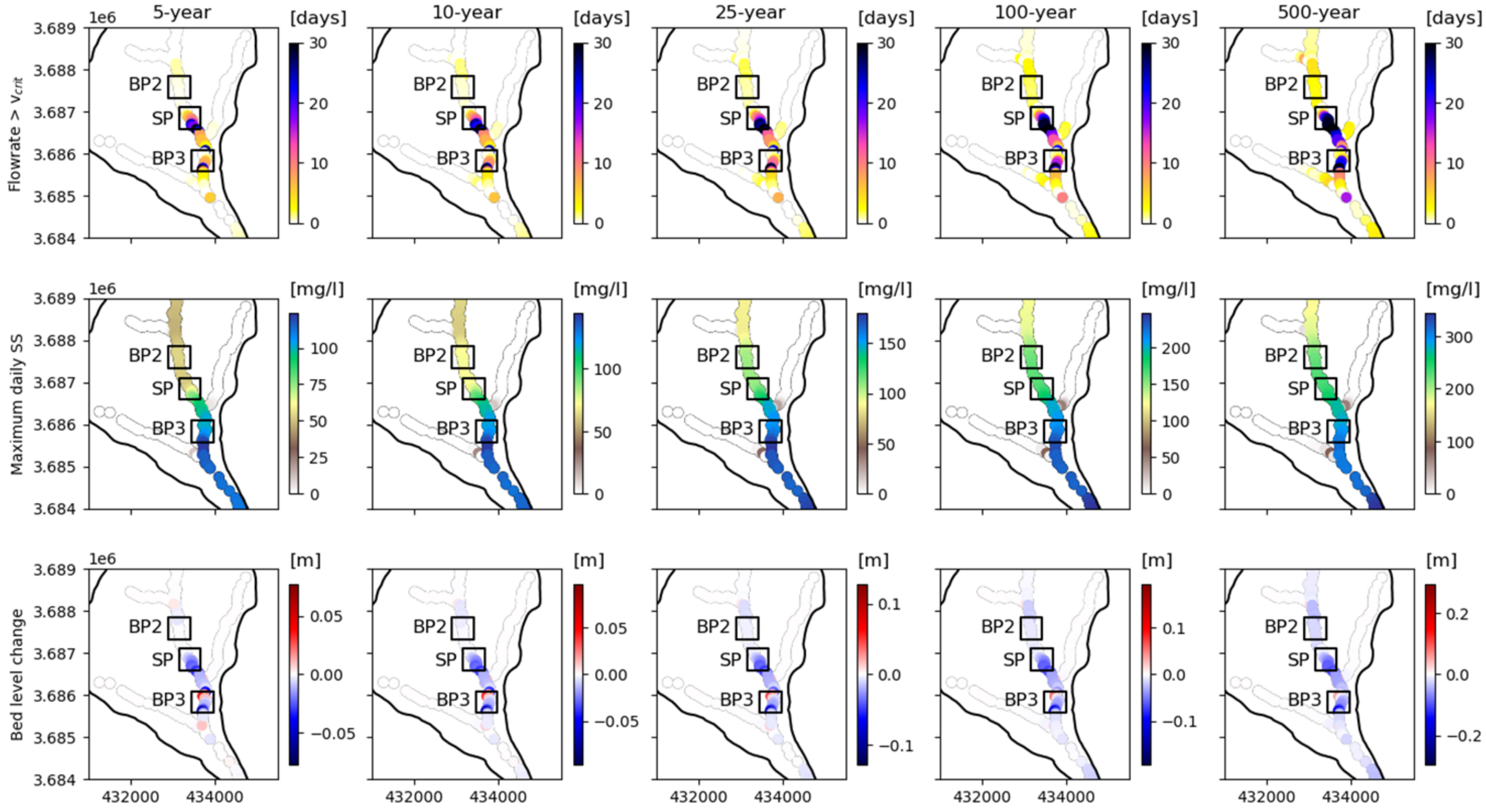
Tims Branch Simulated Discharge and Transport Response – 24-hour event



Subtask 3.1: Calibration of the Tims Branch Watershed Model and Scenario Analysis

FIU Year 3 Research Highlights & Accomplishments:

Tims Branch Simulated Discharge and Transport Response – 24-hour event



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Subtask 3.1: Calibration of the Tims Branch Watershed Model and Scenario Analysis

FIU Year 3 Projected Scope

- Complete simulations and evaluation of event-based uranium transport model for Tims Branch (Milestone 2022-P2-M11).
  - Task delayed.
  - Software and license upgrade in progress.
  - Reforecast from 7/14/2023 to end of September.
- Complete draft manuscript on uranium transport model for Tims Branch (Milestone 2022-P2-M14).
  - Reforecast to FIU Year 4.
- Prepare draft report on evaluation of long-term hydrological response and its impact on U transport in Tims Branch including identification of the role of climate change (Deliverable 2022-P2-D7).
  - Reforecast to FIU Year 4.

FIU Year 4 Proposed Scope

- Complete analysis of results from long-term U transport simulations aimed at evaluating potential impact of seasonal and annual climate variability on U transport in Tims Branch watershed.
- Develop manuscript with DOE-EM collaborators to be published in relevant peer reviewed journal.
- Subtask to be closed out in Year 4. Discussions will be held with SRNL, SRS & DOE-EM HQ collaborators to determine the method of transfer of model and its results to DOE and/or whether there is a need to perform additional scenario analyses utilizing the model in its current state.

Subtask 3.2: Model Development for Fourmile Branch with Specific Focus on the F-Area Wetlands

FIU Applied Research Center

FIU Year 3 Research Highlights & Accomplishments:

Subtask 3.2.1 (Fourmile Branch MIKE Watershed-scale Model):

Problem:

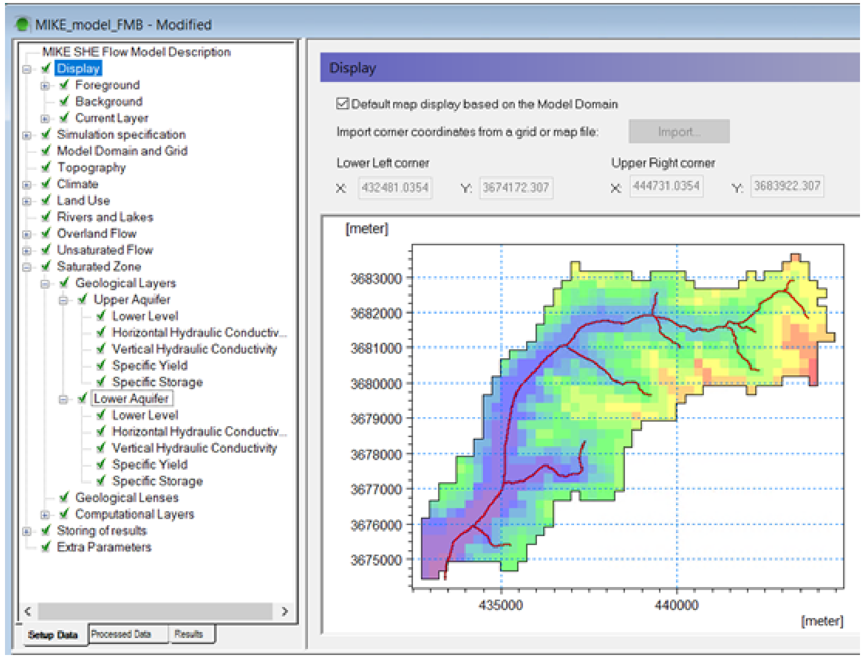
- Historical nuclear waste in surface & subsurface areas of FMB.
- Knowledge gap w.r.t. potential impact of intense precipitation & long-term changes in climate on fate & transport of heavy metals and radionuclides.

Objective:

- Develop **MIKE** hydrological model to simulate surface hydrology in FMB.
- Estimate SW flow with focus on GW-SW interactions in F-Area wetlands.
- Examine seasonal & yearly hydrological variability in FMB.

Results:

- Developed MIKE SHE/MIKE 11 model for FMB watershed (250m res) using open-source data, GIS & Python scripts (Milestone 2022-P2-M2).
- Includes estimates of subsurface parameters for lateral GW flow (upper 2 aquifer systems above Gordon confining unit only), based on literature that showed deeper aquifer systems do not drain into FMB river network.
- Parameter values (e.g., lateral conductivity), derived from documents provided by DOE collaborators.
- For unknown parameters, values originally estimated for MIKE SHE/MIKE 11 Tims Branch model developed under Subtask 3.1 were used.



Overview of the MIKE SHE/MIKE 11 model for Fourmile Branch watershed.

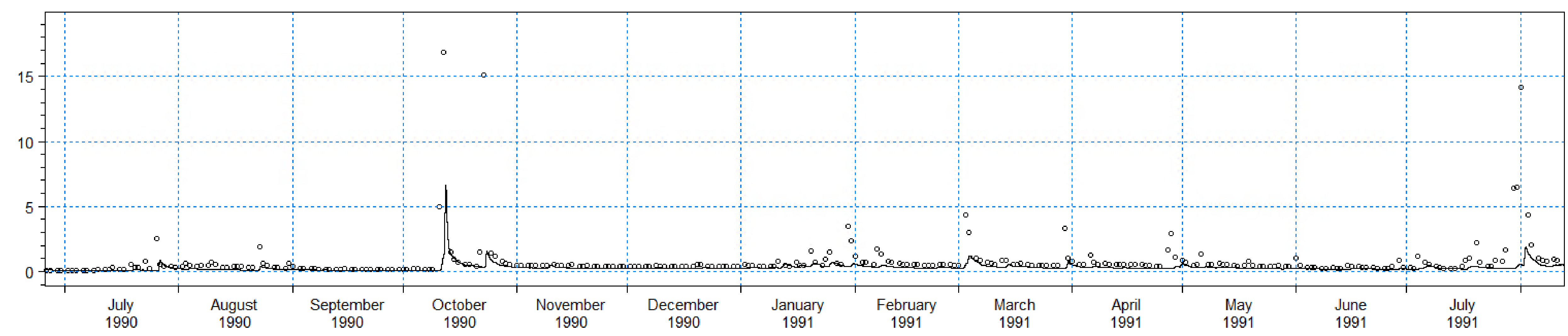
FIU Applied Research Center

Subtask 3.2: Model Development for Fourmile Branch with Specific Focus on the F-Area Wetlands

FIU Year 3 Research Highlights & Accomplishments:

Subtask 3.2.1 (Fourmile Branch MIKE Watershed-scale Model):

- Currently in the process of calibrating the model parameters and perform long-term simulations
- Resolved several errors in the previously developed MIKE model for Fourmile Branch.



Simulated and observed results – discharge at outlet

Subtask 3.2: Model Development for Fourmile Branch with Specific Focus on the F-Area Wetlands

FIU Year 3 Research Highlights & Accomplishments: Subtask 3.2.2 (F-Area ATS Model)

Problem:

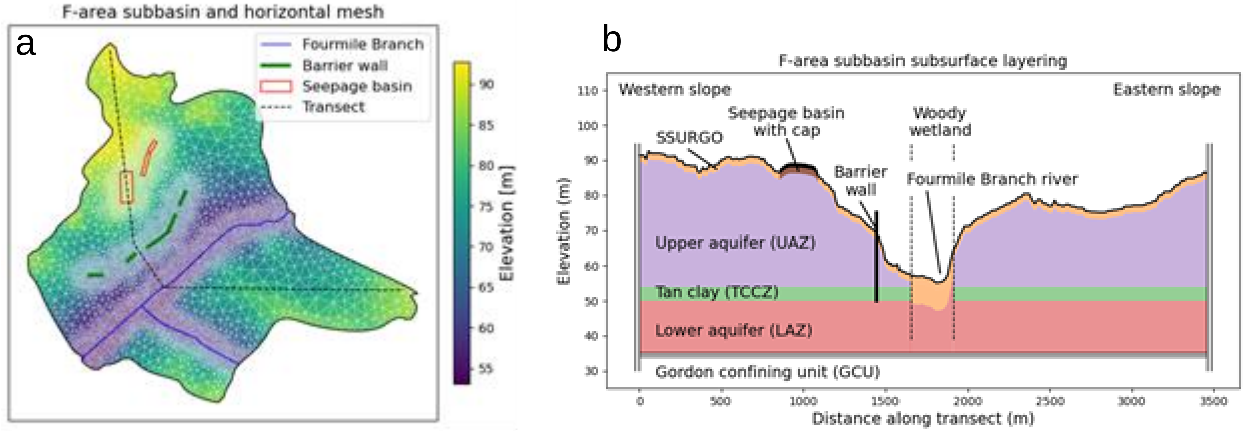
- Uncertainty of conditions influencing contaminant flux in braided wetland system of SRS F-Area and impact of wet & dry condition variability at event & seasonal timescales on contaminant release into FMB stream. *(Particular interest in GW-SW water interactions in F-Area wetlands).*

Objective:

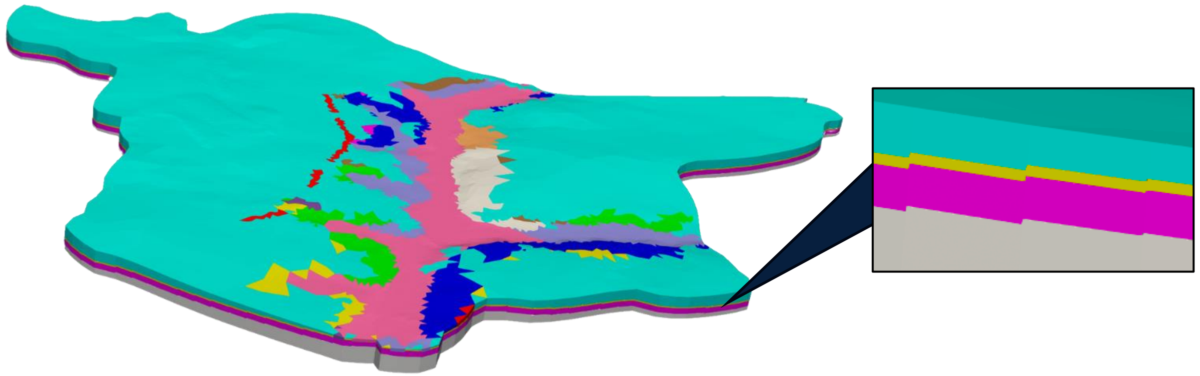
- Develop hydrological model of F-Area (extended beyond seepline and FMB stream) using **Advanced Terrestrial Simulator (ATS)** and perform hydrological simulations at event & seasonal timescales on FIU's HPC.

Results:

- Developed integrated surface-subsurface model of F-Area using ATS (Milestone 2022-P2-M7) and Python package Watershed Workflow, which enables quick generation of ATS model from publicly available data.
- Python scripts developed to generate input files: high-res. mesh of F-Area (NLCD land cover, SURRGO soil texture & subsurface information), daily atmospheric forcing (precip,, temp., rad.) using DayMet data, model input XML file (file info., domain & parameter values, and simulation requirements).
- XML file also contains vegetation characteristics, porosity, residual saturation, thickness, van Genuchten parameters, subsurface soil layer depths, permeability, and watershed delineation lines.



(a) ATS mesh using Watershed Workflow and F-Area boundary shapefile from 10m DEM. FMB river, barrier wall and seepage basins also shown.
(b) Elevation variability along dashed line shown in (a), subsurface layers included in model, depth of seepage basin and barrier wall.
(Tan clay aquitard removed below riverbed as observations show it is non-existent within this domain of the landscape).



3D view of lateral image shown in Fig. 3-6b. Top: SSURGO soil units, barrier wall & seepage basins. Below SSURGO soil units: UAZ (blue), TCCZ (yellow) and LAZ (pink) layers, assumed to be rested on top of impermeable layer (gray).

Subtask 3.2: Model Development for Fourmile Branch with Specific Focus on the F-Area Wetlands

FIU Year 3 Projected Scope

Subtask 3.2.1:

- Perform hydrological simulations & initiate calibration of any remaining unknown parameters using flow observations in FMB (Milestone 2022-P2-M13).

Subtask 3.2.2:

- Perform historical simulations and include upstream river network boundary conditions to enable inflow from upstream rivers into riparian zone domain. Use model to evaluate impact of seasonal & decadal variations in weather (including climate change) on hydrology and GW-SW interactions in F-Area wetlands.
- Research supports Advanced Long-Term Environmental Monitoring Information Systems (ALTEMIS) program in SRS F-Area. Model simulations will give a better understanding of how temporal variability of moisture conditions at seepline interface likely affects redox and microbial processes and how this ultimately impacts contaminant mobility.
- Develop report on F-Area model simulations using ATS and evaluate seasonal variation in SW-GW interaction within the seepline/riparian zone interface (Deliverable 2022-P2-D5).

FIU Year 4 Projected Scope

- Complete calibration of MIKE model and perform hydrology simulations (event-based & long-term) at FMB watershed scale.
- Calibrate ATS model using in-situ sensor network data and perform hydrology simulations (event-based & long-term) in F-Area seepage face and riparian zone adjacent to braided FMB river network.
- Train FIU graduate and/or undergraduate students (DOE Felllows) on model development using MIKE and ATS, as well as data generation and model evaluation using GIS and Python.
- Develop model code for U/I-129 transport in close collaboration with ALTEMIS project team members and perform preliminary simulations of flow and reactive transport of U/I-129 in SRS F-Area.

Task 5

Research and Technical Support for WIPP

Applied Research Center

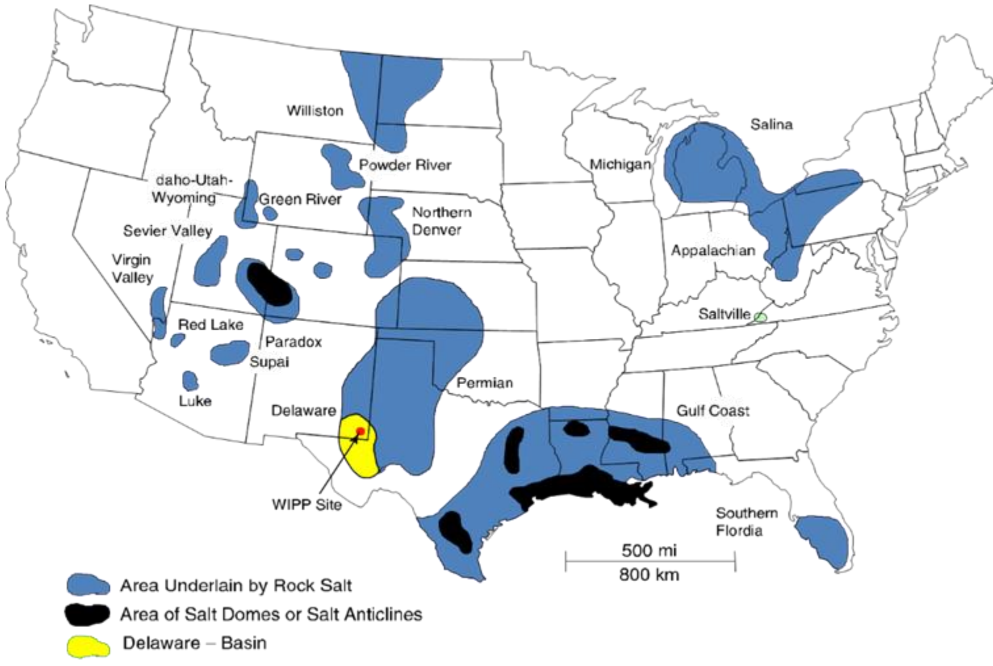
Subtask 5.1: The Fate of Actinide in the Presence of Ligands in High Ionic-Strength System

Site Needs:

- There is a critical need by DOE to understand the long-term storage of nuclear waste in the Waste Isolation Pilot Plant (WIPP) is in compliance with Federal regulation and protective of human health and the environment.
- Thus, safety assessment (SA) is required for recertification of the WIPP every 5 years.
- A better understanding of the fate and transport of actinide in a high ionic-strength brine environment is important to addressing the low-probability scenario of potential brine inundation and contaminants' release due to human intrusions.

Objectives:

- The role of corrosion products such iron oxide minerals (e.g., pyrite) and cellulose degradation product, (isosaccharinate [ISA]) that may enhance actinide solubility is poorly understood.
- Investigate via batch sorption experiments actinide interaction with brines in environments expected at the WIPP.



The WIPP site, near Carlsbad, NM

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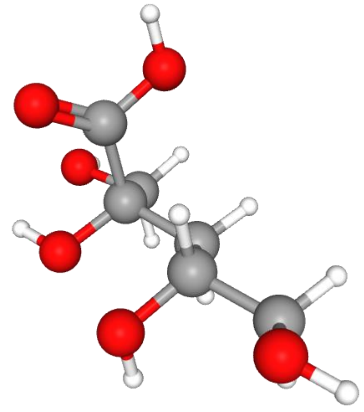
Subtask 5.1: The Fate of Actinide in the Presence of Ligands in High Ionic-Strength System

FIU Year 3 Research Highlights & Accomplishments:

- The impact of ISA on sorption of actinide onto iron oxide mineral (pyrite, FeS_2) was studied under anaerobic conditions.
- Pyrite – powder, particle size: ~45 µm
- UO_2^{2+} and, Nd^{3+}, Th^{4+}, were used as stable chemical analogs for americium and plutonium.
- An actinide concentration used in these studies: ~10^{-7} M.
- Brines concentration & type: 0.1, 1.0 and 5.0 mol/L NaCl, KCl, $MgCl_2$ and $CaCl_2$.
- Batch experiments:
  - 1-10 g/L pyrite and 5 x10^{-4} mol/L NaISA, ($NaC_6H_{11}O_6$)
  - Spiked samples were pH adjusted to a pH value of 8 ±0.5.
  - Centrifuged at 8000 RPM for 20 min using 10K MWCO device.
  - All batch experiments were performed in triplicates with standard deviations <10%.
- Samples were collected at various time intervals and analyzed on the ICP-MS.

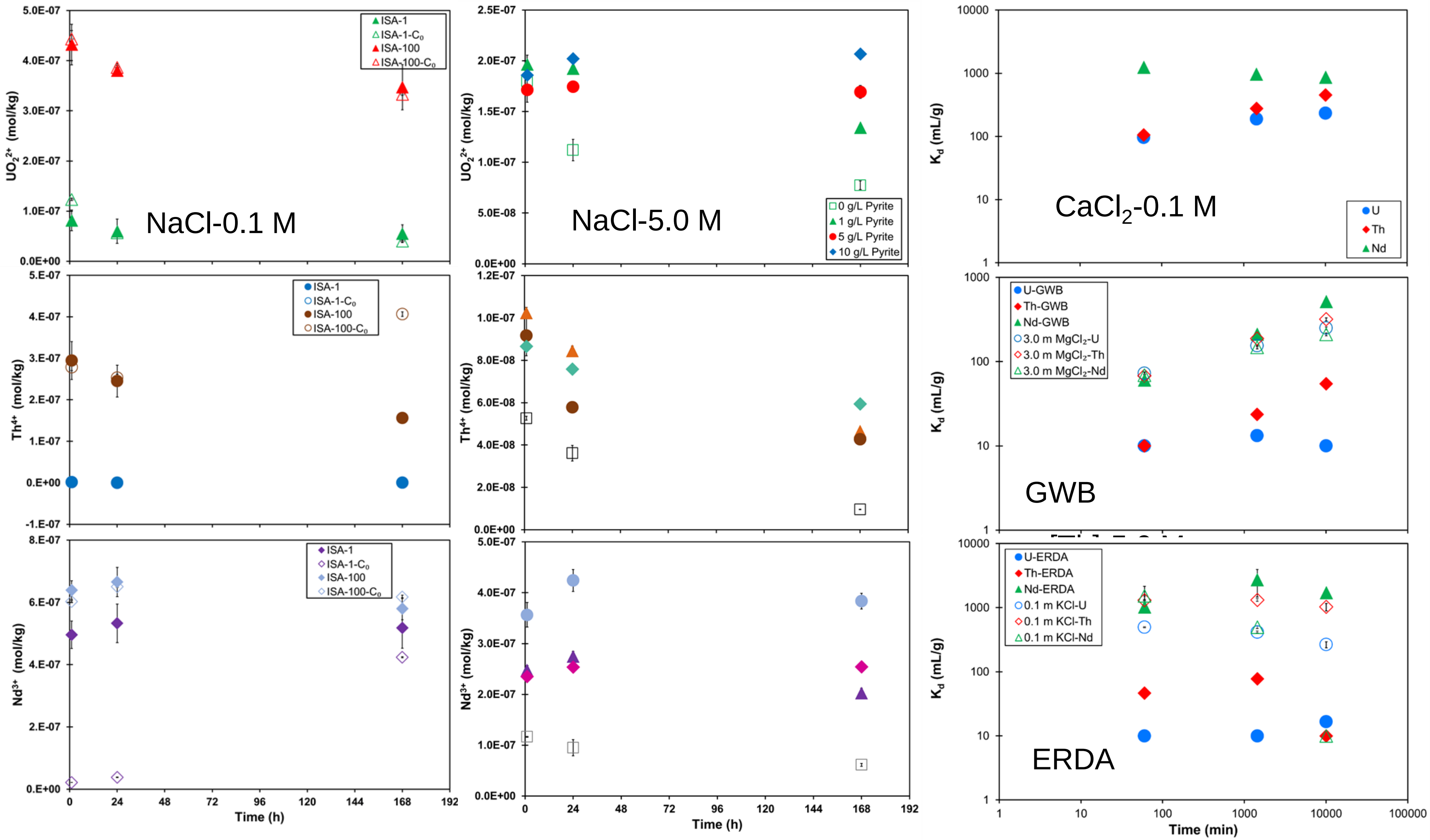


Applied Research Center

Subtask 5.1: The Fate of Actinide in the Presence of Ligands in High Ionic-Strength System

FIU Year 3 Research Highlights & Accomplishments:

- ISA (100 mg/L) enhanced actinide solubility
- Increasing pyrite dosage and ISA impacted solubility of UO_2^{2+} and, Nd^{3+}, Th^{4+} via changes to solution pH.
- Sorption of Nd^{3+} was typically larger compared to sorption of UO_2^{2+} and Th^{4+}



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Subtask 5.1: The Fate of Actinide in the Presence of Ligands in High Ionic-Strength System

FIU Year 3 Research Highlights & Accomplishments:

- Completed batch sorption experiments investigating the impact of ISA on actinide sorption onto pyrite in WIPP-relevant brines such as NaCl, $MgCl_2$, $CaCl_2$, the U.S. Energy Research and Development Administration Well 6 brine (ERDA-6, low Mg) and Generic Weep Brine (GWB, high Mg) using actinide concentration of 10^{-7} M.
- Conference presentation at 2023 Waste Management Symposium and ABC Salt Workshop.

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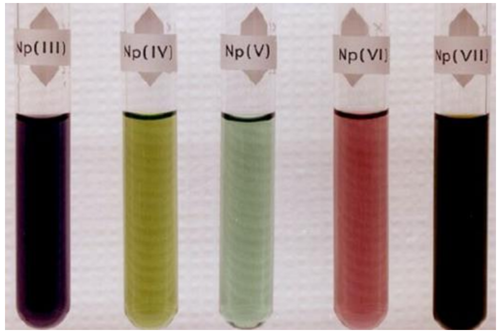
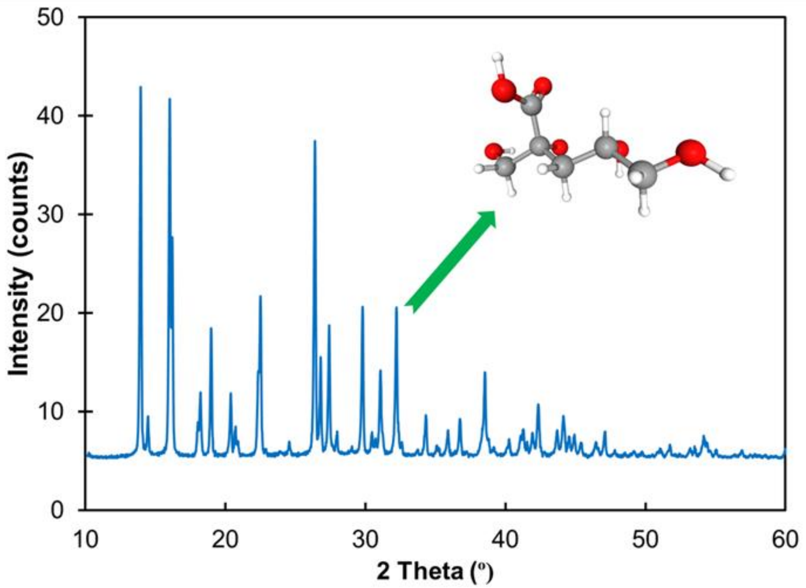
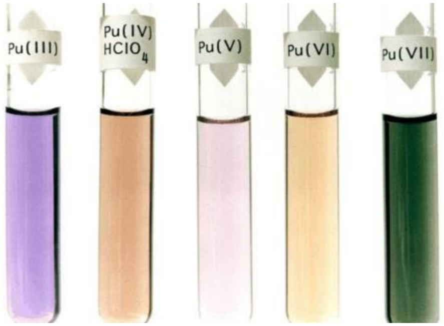
FIU Year 4 Projected Scope

- Employ EQ3/6 v8a speciation model to obtain pertinent Pitzer's interaction parameters (virial coefficients) required for high salt systems.
- Study the impact of citrate, an important byproduct of alkaline degradation of cellulose on sorption of actinide onto iron oxide minerals in WIPP-relevant brines and conditions.
- Characterize treated solid phases employing microscopy, spectroscopy and x-ray diffraction techniques.







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Task 6

Hydrology Modeling of Basin 6 of the Nash Draw Near the WIPP

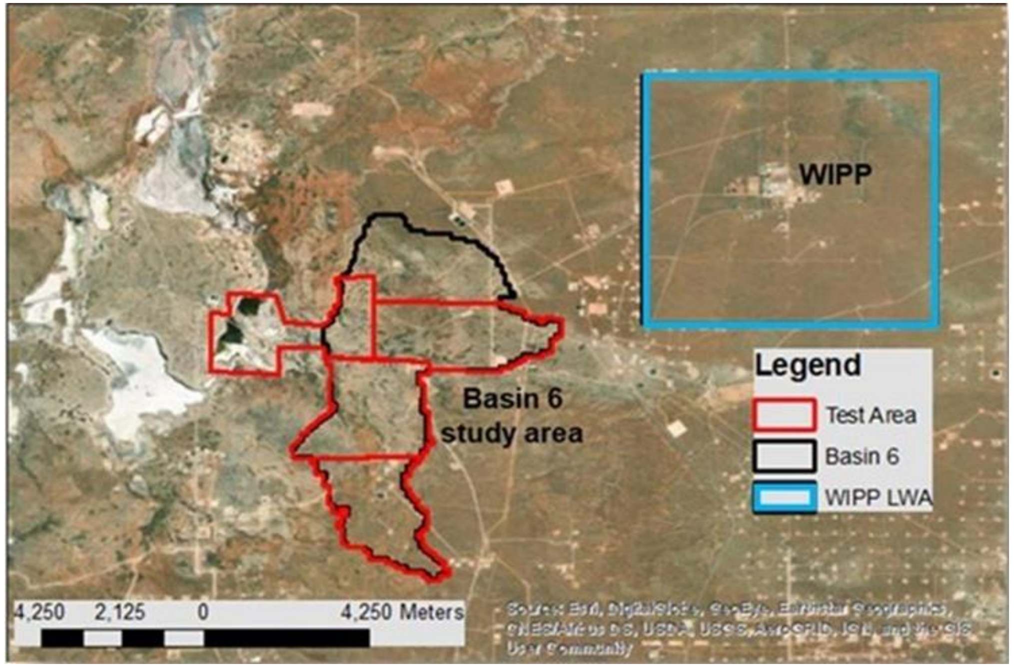
Applied Research Center

Task 6: Hydrology Modeling of Basin 6 of the Nash Draw Near the WIPP

Site Needs:

- Understanding of regional water balance near WIPP, particularly Culebra recharge, during intense, episodic precipitation events
- Estimation of propagation rate of shallow dissolution front.
- Assessment of impact of land-use changes around WIPP on water levels in compliance-monitoring wells.
- A high-resolution DEM that can represent localized features (i.e., along river network, in gullies and sinkholes) where recharge anticipated to predominantly occur.

Basin 6 study area west of the WIPP, NM.



Objectives:

- Subtask 6.1: Develop high-res. (1m) DEM of Basin 6 of the Nash Draw near the WIPP (completed in FIU Year 2).
- Subtask 6.2: Use high-res DEM to develop hydrological model of Basin 6 using Advanced Terrestrial Simulator (ATS) to:
  - Compute regional water balance and derive more accurate estimates of GW recharge to better predict propagation rate of shallow dissolution front and potential long-term impact on WIPP repository performance.
  - Evaluate impact of climate change and surface features (e.g., sinkholes and swallets), soil properties, and vegetation on GW recharge.
- Subtask 6.3: Collect field data to support model calibration and validation.

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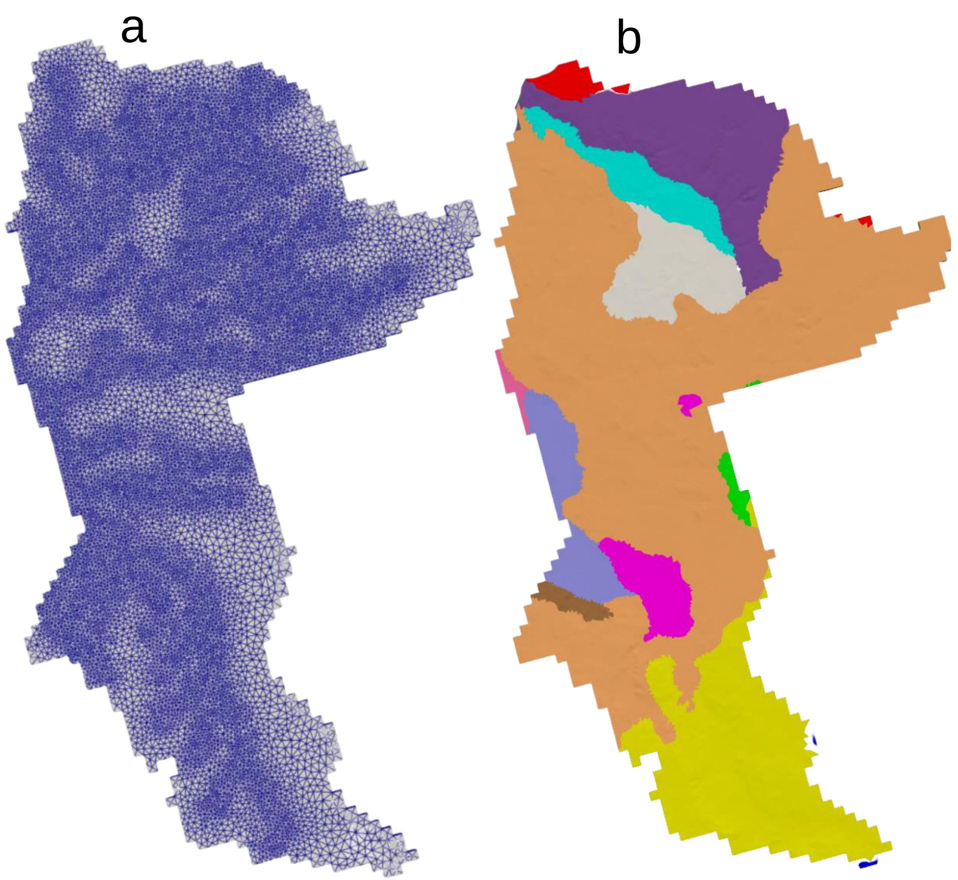
Subtask 6.2: Model Development

FIU Year 3 Research Highlights:

- Implemented Python package, Watershed Workflow - enables quick generation of a site mesh from publicly available data.
    - High-res. mesh of Basin 6 (includes spatial variations in NLCD land cover types, SURRGO soil texture & subsurface information).
    - Daily atmospheric forcing (precipitation, temperature, radiation) using DayMet data.
- Developed Python scripts to generate input files:
    - Model input XML file (with file information, domain & parameter values, and simulation requirements).
    - Automating the input file generation for more efficient and quicker model building.



(a) ATS mesh of Basin 6 using Watershed Workflow. (b) Colors indicate different SURRGO soil regions representing land surface variability in model.

Subtask 6.2: Model Development

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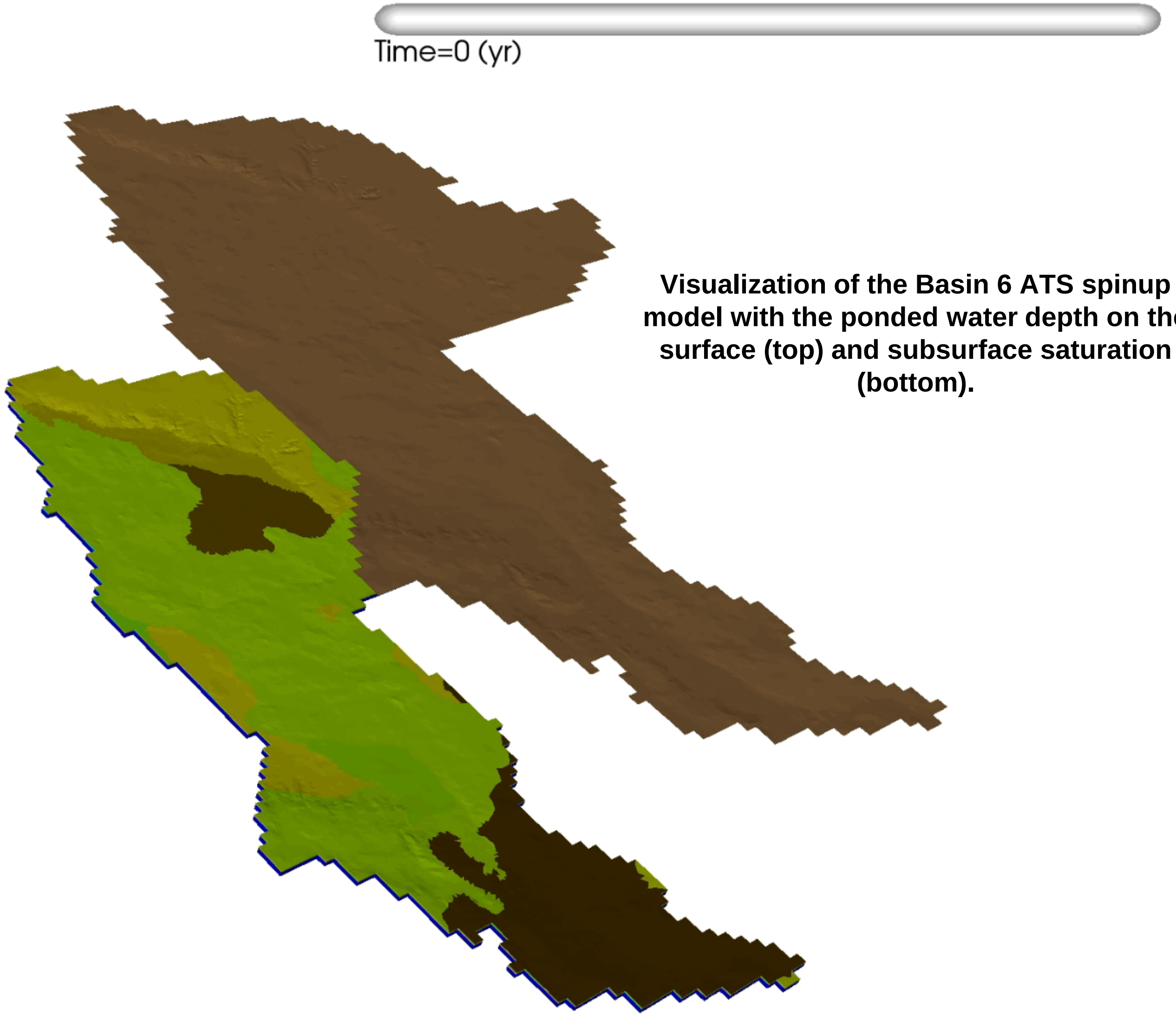
FIU Year 3 Research Highlights:

- Developed an integrated surface-subsurface hydrology model using ATS for the Basin 6 region.
- Developed a spinup model to establish equilibrium in the water balance, in which there was a set water table and constant meteorological forcing.
- Developed a transient model that uses the results of the spinup model to replicate multiple years of actual meteorological forcing data from the region for a certain period of time.
- 2014 is a year of interest due to major flash flooding from two cyclones in SE New Mexico.



Visualization of the Basin 6 ATS spinup model with the ponded water depth on the surface (top) and subsurface saturation (bottom).

Subtask 6.2: Model Development

FIU Year 3 Projected Scope

- Perform multi-year simulations of Basin 6 hydrological response using ATS and draft report on results (Deliverable 2022-P2-D6).
- Incorporate significant surface features (sinkholes & swallets) that increase infiltration and can have impact on regional GW recharge.
- Calibrate model using data collected during summer of 2023.
- Use calibrated model to evaluate impact of seasonal & decadal variations in weather (including climate change) on regional hydrology & GW recharge, so DOE-EM can better predict rate of halite dissolution and propagation of shallow dissolution front so potential impact on WIPP performance can be quantified.

FIU Year 4 Projected Scope

- Calibrate model and perform hydrology simulations (event-based & long-term) in Basin 6 using ATS and field observations obtained in FIU Year 3 as part of Subtask 6.3.
- Perform scenario analyses with sinkhole implementation & incorporation of field data.

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Subtask 6.3: Fieldwork and Data Collection to Support Hydrological Model Calibration and Validation (NEW)

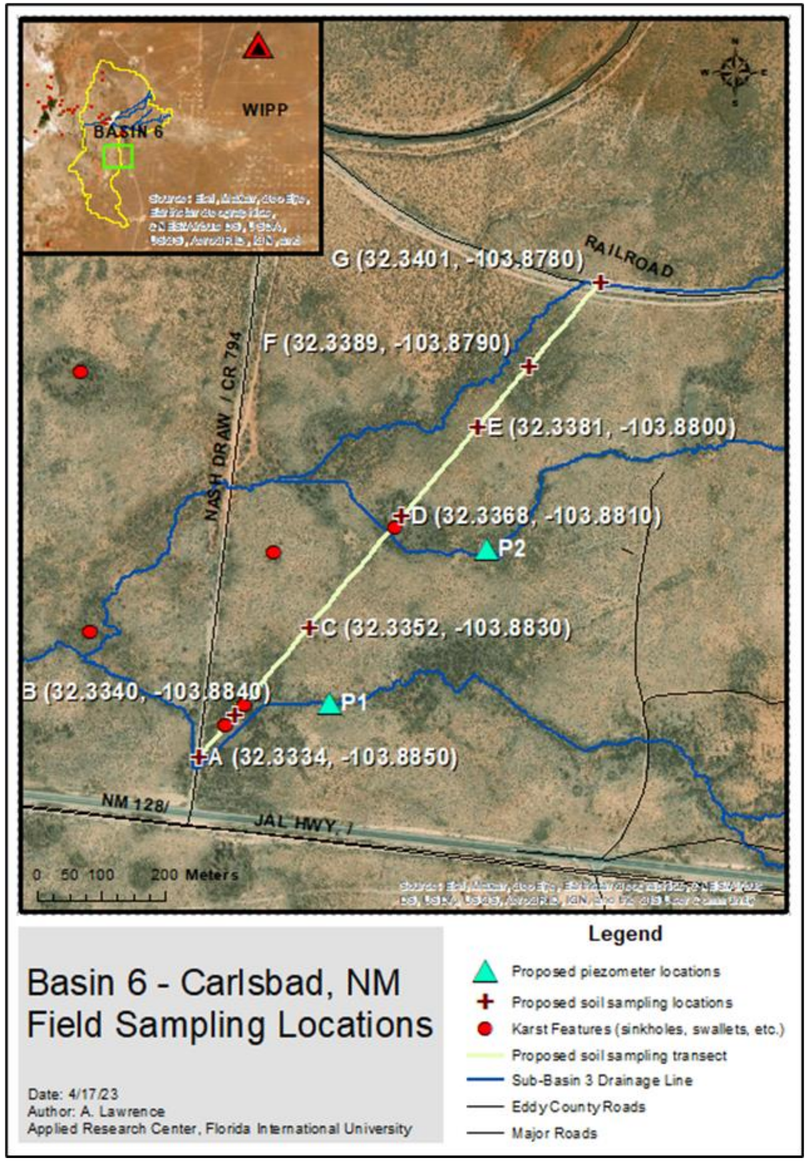
FIU Year 3 Research Highlights:

Background:

- In-situ observations of soil texture, organic content, and soil physical properties, and information on where surface flow occurs currently unavailable for Basin 6 (*potentially impact flow of water in subsurface*).
- Information from soil pits nearby or large-scale soil texture datasets available, but unknown how representative they are for Basin 6.
- Specific location and magnitude of surface flow in Basin 6 is needed to evaluate performance of the ATS model developed.

Objectives:

- Collect surface soil samples and perform lab analyses to obtain soil texture information for various locations and at various depths in Basin 6.
- Deploy water level monitoring devices in Basin 6 to obtain specific location and magnitude of surface flow as forced from intense precipitation events (part of the North American Monsoon).
- Use field data for model calibration & validation, to assess performance of Basin 6 ATS model developed in Subtask 6.2.
- Use soil texture observations to evaluate quality of large-scale publicly available soil texture datasets (STATSGO2, SSURGO and SoilGrids).



Map of field sampling locations.

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Subtask 6.3: Fieldwork and Data Collection to Support Hydrological Model Calibration and Validation (NEW)

FIU Year 3 Research Highlights:

Field work from May 29 – June 1 (Milestone 2022-P2-M12)

- Identified and plotted key locations in Basin 6 along ~1 km transect line for collection of soil samples and deployment of piezometers using ArcGIS tools in ArcMap.
- 5 HOBO U20L water level loggers (pressure transducers) were deployed in Basin 6 study in areas where surface flow is likely to occur.
- 48 soil samples collected at depths from 0 - 10 feet below the ground surface.
- Noted key features along the way in Basin 6.
- Soil properties of interest: particle size distribution, bulk density, porosity, organic content (potentially affect processes such as infiltration, erosion, nutrient cycling, and biologic activity).
- Fieldwork support provided by Dr. Anderson Ward (CBFO) and Dr. Dennis Powers (Consulting Geologist & subject matter specialist on Nash Draw hydrogeology).

Left: **Eijkelkamp soil sampling rings;** ***Right:*** **HOBO water level data logger.**

Collecting soil samples ***(left)*****;**
soil variation near Location 1 ***(right)*****.**

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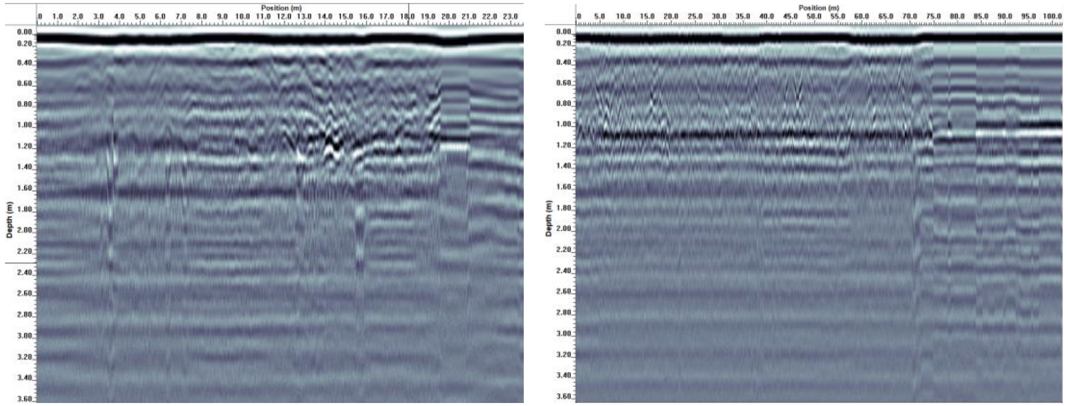
Subtask 6.3: Fieldwork and Data Collection to Support Hydrological Model Calibration and Validation (NEW)

FIU Year 3 Research Highlights:

HOBO water level data logger at two sinkholes.

HOBO water level data logger at a ponding area and its upstream flow path.

Using a GPR rover within Basin 6 to obtain information on subsurface variation in soil characteristics (GPR rover developed in Project 5, Task 2).



Preliminary GPR data.

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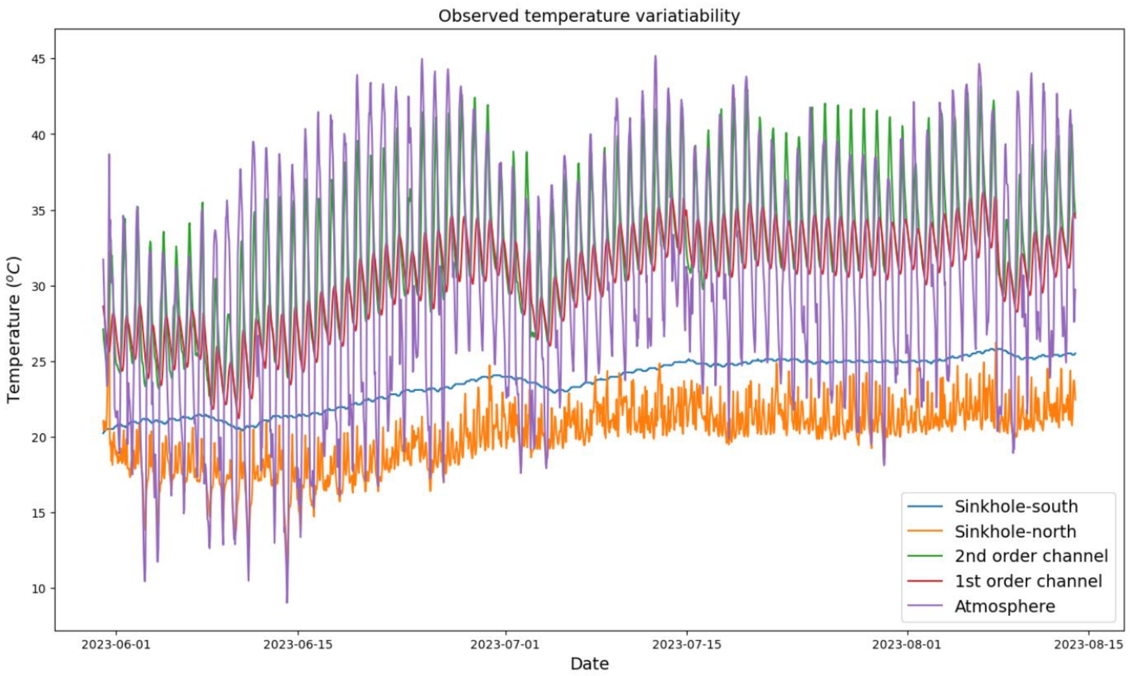
Subtask 6.3: Fieldwork and Data Collection to Support Hydrological Model Calibration and Validation (NEW)

FIU Year 3 Projected Scope

- Download water level data from piezometers deployed in Basin 6 at end of August 2023 and use for model calibration and validation.
- Initiate soil analysis & comparison of soil texture data with national databases (STATSGO, SSURGO, SoilGrids). This effort will extend into FIU Year 4.



FIU Year 4 Projected Scope

- Continue analysis of soil samples collected in Summer 2023.
- Collect and analyze additional soil samples at different depths throughout Basin 6.
- Collect additional water level measurements at sites previously monitored in FIU Year 3 and extend water level sensor network to include sinkholes along main river network and at basin exit near brine lakes.
- Take infiltration measurements at several locations throughout the basin.

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Task 7

Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

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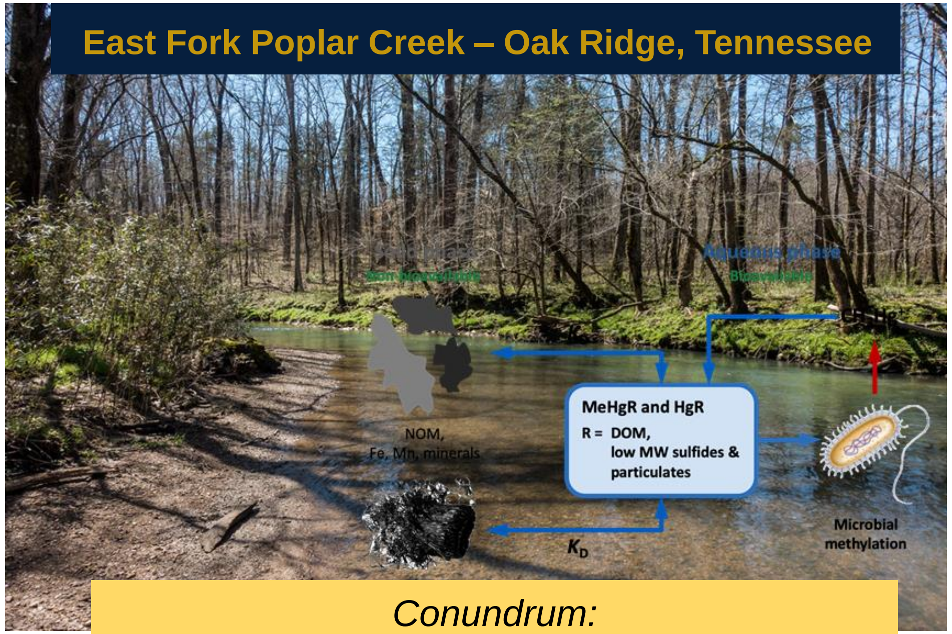
Task 7: Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

Site Needs:

- The complex geochemistry of mercury renders its cleanup a challenging and costly endeavor for increasing numbers of mercury-contaminated sites globally.
- Widespread uses of Hg have led to diffuse sources that further complicate remediation efforts for Hg in freshwater systems, such as the East Fork Poplar Creek (EFPC) in Oak Ridge, Tennessee.
- EFPC is a 26-kilometer low gradient stream contaminated with Hg from past weapon development efforts at the Y-12 (National Security Complex) during the 1950s. Mercury releases persist from point and diffuse sources.



Conundrum:
Hg fate and transport within EFPC ecosystem are controlled by its strong interaction with dissolved organic matter (~3 mg/L DOM at baseflow), which renders its sorption to sorbents and removal from the water column by strong reductants problematic.

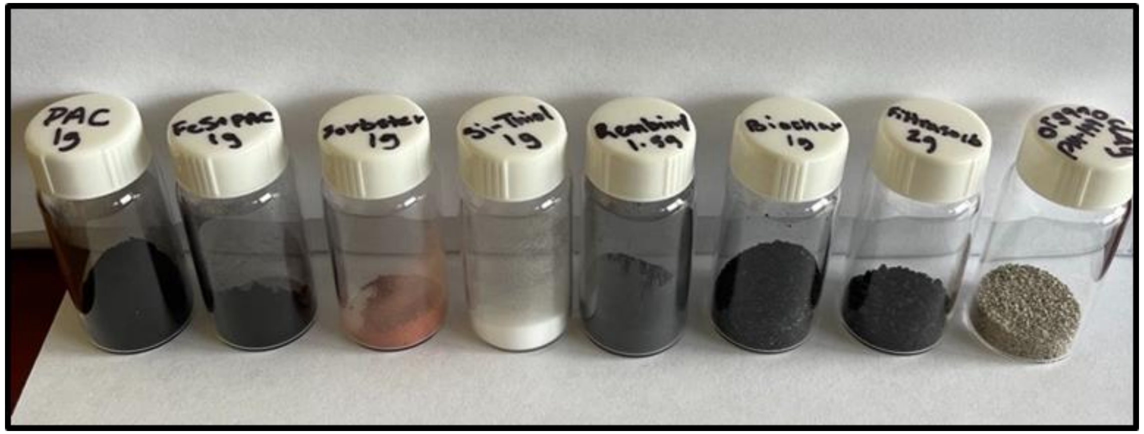
Objectives:

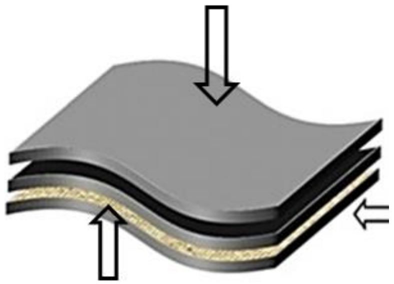
- Evaluate a suite of engineered sorbents for mercury removal in a freshwater system such as that of EFPC. Formation of Hg–DOM complexes in EFPC is problematic for remedial technology.
- Develop effective, remedial technology consisting of Hg-sequestrating sorbents stacked between layers of porous geotextile mats.

Task 7: Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

FIU Year 3 Research Highlights & Accomplishments:

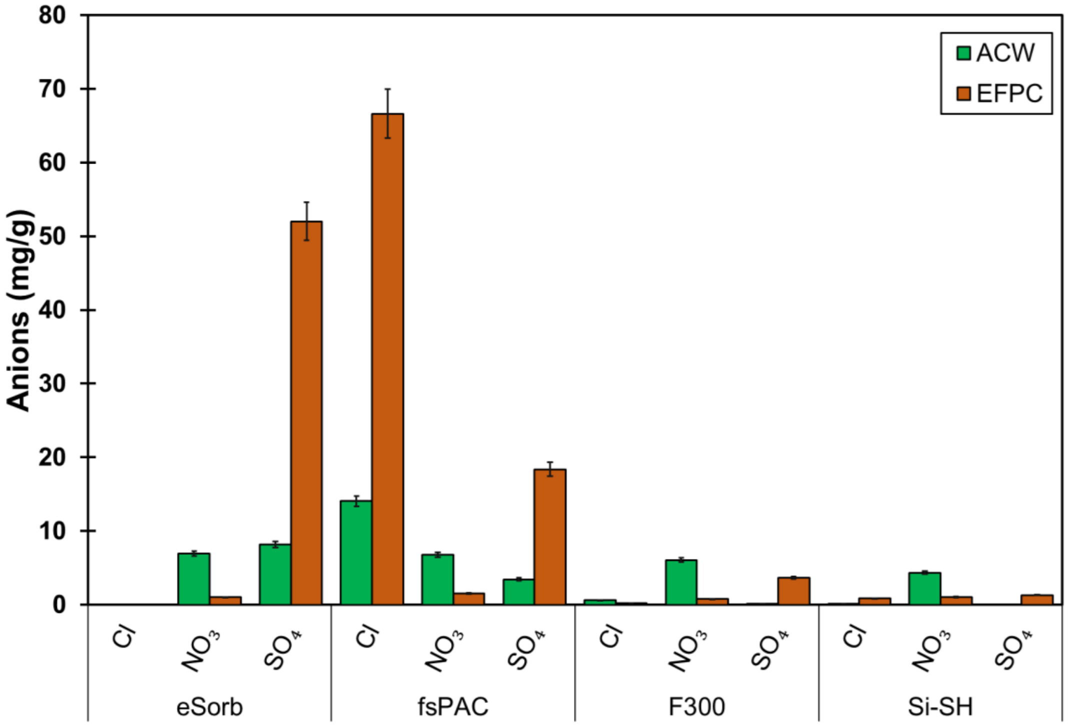
- Performed stability evaluation of select sorbents via EPA's Toxicity Characteristic Leaching procedure (TCLP), SW-846 Test Method 1311 and leaching test to determine release of constituents from sorbent media.
- Eight sorbents were studied as potential sorbents for in-situ remediation of mercury species in EFPC ecosystem.
  - Sorbent media were mostly carbon-based materials or functionalized silica/clays.
  - All batch experiments were performed in using ACW and actual EFPC water
- Evaluated materials: *Biochar (PBC); Sorbster (eSorb); Si-thiol (Si-SH); Mackinawite blended powdered activated carbon (fsPAC); Powdered activated carbon (nsPAC); Organoclay PM-199 (Q-Clay); Filtrasorb 300 (F300) and RemBind (eBind).*

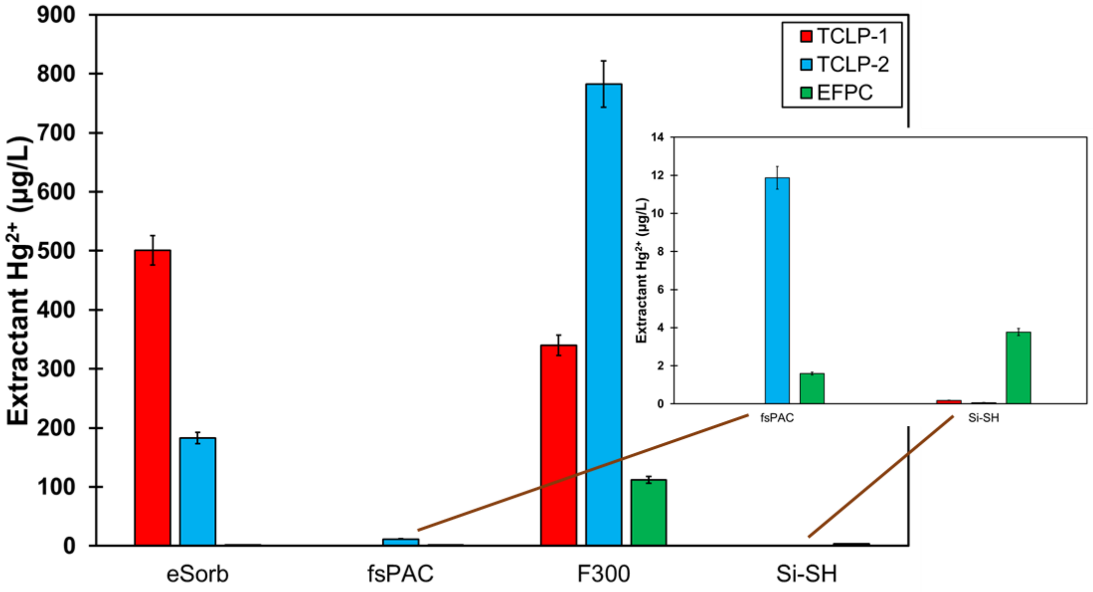




Task 7: Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

FIU Year 3 Research Highlights & Accomplishments:





- *Si-SH* and *F300* leached anions (Cl^-, NO_3^-, and SO_4^{2-}) that were generally minimal and would not major impact on mercury biogeochemistry (left). *eSorb* and *F300* leached the highest amount of Hg^{2+} compared to the fsPAC and Si-SH media (right).

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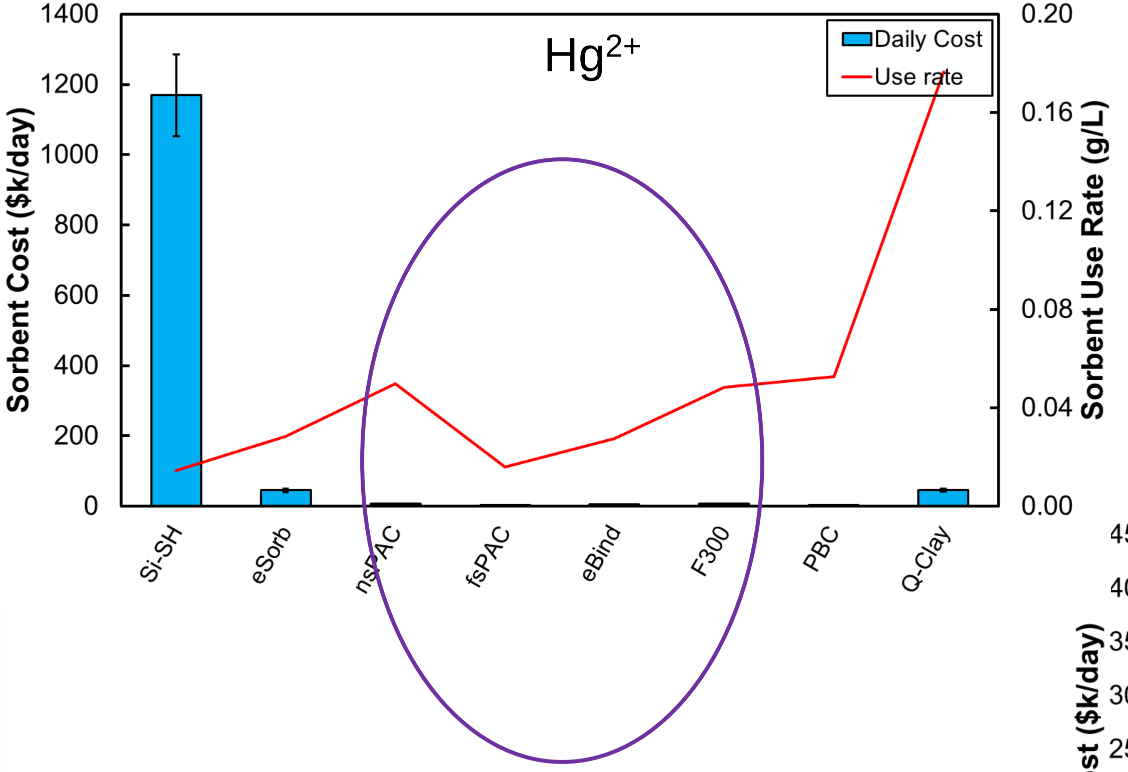
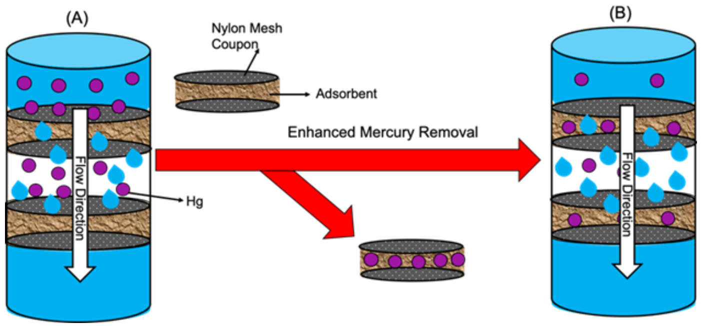
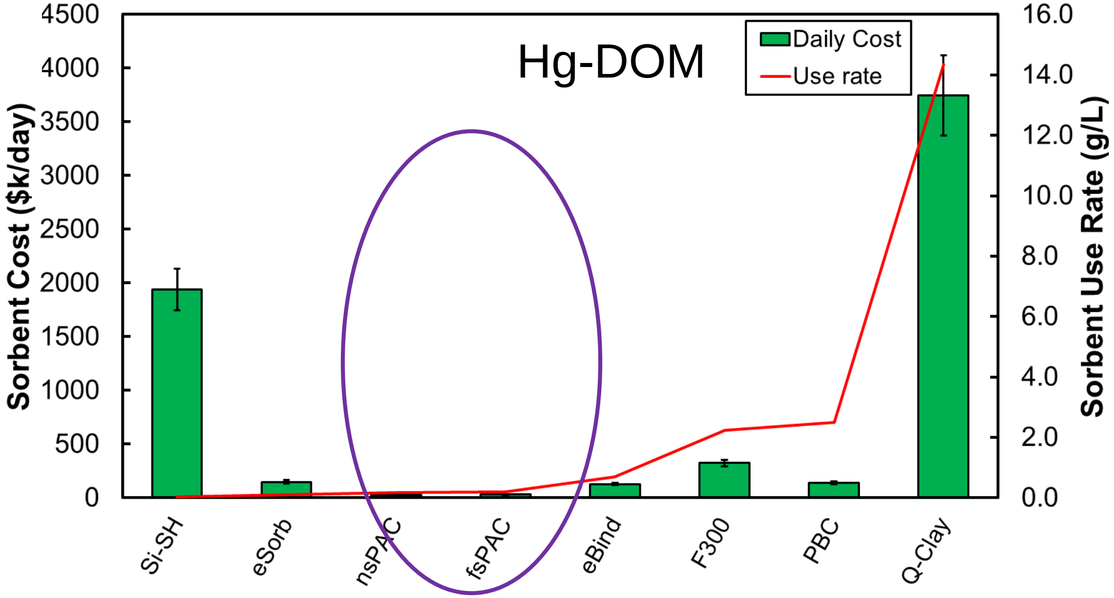
Task 7: Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

FIU Year 3 Research Highlights & Accomplishments:





In the absence and presence of DOM, fsPAC and nsPAC sorbents afforded the most cost-effective remedial solution for mercury



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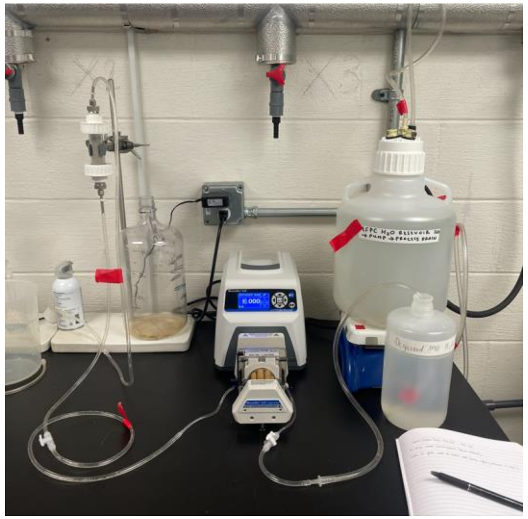
Task 7: Engineered Multi-Layer Amendment Technology for Hg Remediation on Oak Ridge Reservation

FIU Year 3 Research Highlights & Accomplishments:

- Poster presentations at the 2023 Waste management symposium.
- Caridad Estrada, the DOE Fellow supporting this subtask gained admission to Princeton University to conduct doctoral studies in Environmental Engineering.

FIU Year 4 Projected Scope

- Determine physiochemical properties of Hg sorbents upon contact with environmental media (DI Water, ACW, EFPC water) and characterize pristine and treated sorbents using microscopy and spectroscopy techniques.
- Conduct comprehensive column studies with select sorbent media to elucidate mercury sorption under conditions representative of EFPC site.



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FIU Year 3 Overall Accomplishments

Highlights

Graduated DOE Fellows:

- Stevens Charles - BS, Civil Engineering (pursuing MS in Env. Engineering at Univ. of Georgia)
- Gisselle Gutierrez-Zuniga - MS, Environmental Engineering (accepted position as Civil Analyst at Kimley-Horn & Assoc., Inc.)
- Phuong Pham - PhD, Chemistry (accepted position as Postdoctoral Associate at SRNL)
- Caridad Estrada - BS, Environmental Engineering (pursuing PhD in Env. Engineering at Princeton Univ.)
- Juan Morales - PhD, Env. Health Sciences (expected grad. 2024) (brief emp. at SRNL before joining US Navy at Cherry Point)
- Mariah Doughman - PhD, Chemistry (expected grad. 2024, accepted into the Department of Energy Office of Environmental Management Minority Serving Institutions Partnership Program Graduate Fellowship at PNNL)

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FIU Year 3 Overall Accomplishments

Highlights

Conference papers & oral presentations:

WM23

- Student Track (DOE Fellows) - 4 posters by Aubrey Litzinger, Caridad Estrada, Mariah Doughman and Phuong Pham
- Professional Track - 1 poster by John Dickson, 1 oral presentation by Yelena Katsenovich.

Remplex

- Abstracts for 2 posters accepted by Mariah Doughman and Yelena Katsenovich.

Peer review publications:

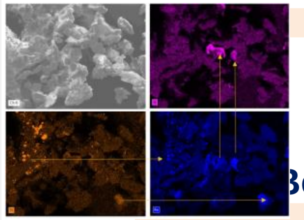
- Kaplan, D. I., R. J. Smith, C. J. Parker, K. A. Roberts, P. Hazenberg, J. Morales, E. J. O'Loughlin, M. I. Boyanov, P. Weisenhorn, K. M. Kemner, and B. A. Powell, 2023: Natural attenuation of uranium in a fluvial wetland: Importance of hydrology and speciation, *Applied Geochemistry*, 155, 105718, doi: 10.1016/j.apgeochem.2023.105718.
- *In preparation for submission to Journal of Hydrology:* Zhou, Y., Alam, M., Lawrence, A., Morales, J., Looney, B. B., Seaman, J. C., Kaplan, D., Parker, C.J., Lagos, L. and P. Hazenberg. (2023) Hydrologic Model Development to Understand Flow and Shear Stress Variability during Extreme Precipitation Events in the Tims Branch Watershed, SC.
- *Prepared for the submission to J. Env Management:* Doughman, M., Katsenovich, Y, O'Shea, K, Hilary P. Emerson, H. P. , Szecsody J, Kenneth Carroll, K, and N. Qafoku, "Impact of Chromium (VI) as a Co-Contaminant on the Sorption and Co-Precipitation of Uranium (VI) in Sediments Under Mildly Alkaline Oxic Conditions"
- *Prepared for submission to Corrosion Science*: Katsenovich, Y, Drozd, V, Shambhu Kandel, S, Lagos, L, and M. Asmussen, The corrosion behavior of borosilicate glass in the presence of cementitious waste forms.
- *In preparation for submission* by J. Dickson et al., Engineered Media for Mercury Removal in the Presence of Dissolved Organic Matter.

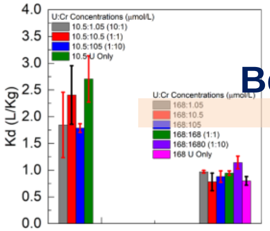
FIU Applied Research Center

Technology Development and Deployment Road Map

Technology	2020	2021	2022	2023	2024
Hanford: In Situ Sequestration	Bench-scale testing	Bench-scale testing	Bench-scale testing	Bench-scale testing	Knowledge transfer to support eval. of treatment options of select zones in Central Plateau Subsurface (200-DV-1 Treatability Studies)
Hanford: Natural Attenuation	Bench-scale testing	Bench-scale testing	Bench-scale testing	Bench-scale testing	Knowledge transfer to support Modeling for No-Treatment or MNA Scenario across multiple locations on Central Plateau
Hanford: Glass Waste Forms	Bench-scale testing via SPFT	Bench-scale testing via SPFT	Bench-scale testing via SPFT/ PCT	Bench-scale testing via SPFT/PCT	Bench-scale testing via PCT; Knowledge transfer to support PA of WRPS Field Lysimeter Test Facility & ILAW glass testing programs; DOE-EM R&D Roadmap

Science to Support Technology Deployment (In Situ Sequestration, 2020–2021)





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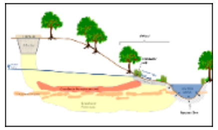
Technology Development and Deployment Road Map

Technology	2020	2021	2022	2023	2024
SRS/SRNL	Fundamental Science to Support Technology Deployment for SRS Area Completion Project				
Environmental factors controlling contaminants at SRS 	Bench-scale experiments	Bench-scale experiments	Bench-scale experiments	Bench-scale experiments	Knowledge transfer for long-term monitoring
Evaluation of Humic Acid for uranium sequestration 	Bench-scale experiments	Bench-scale experiments	Bench-scale experiments	Bench-scale experiments	Knowledge transfer for long-term monitoring
Mercury ORNL 	Conceptual Design of Technology	Bench-Scale Testing	Bench-Scale Testing	Bench-Scale Testing	Knowledge transfer to support tech. selection for Hg remed. at ORR
WIPP 	Bench-Scale Testing	Bench-Scale Testing	Bench-Scale Testing	Bench-Scale Testing	Knowledge transfer to support site safety and performance assessment for WIPP

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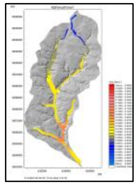
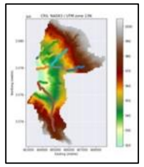
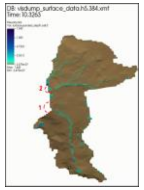
Technology Development and Deployment Road Map

	Technology	2020	2021	2022	2023	2024
SRS		Tims Branch Model: Integrated SW/GW Model Calibration	Sed. Transport Model Calibration/ Validation	Contaminant Transport Model Calib./Validation	Model Implementation/ Hand-over	
SRS		Fourmile Branch Model: Conceptual Model Development	Conceptual Model Development	Integrated SW/GW Model Dev. & Calib.	Sed./Contam. Transport Model Calib./Validation	Model Implementation/ Hand-over
WIPP (Basin 6)		Basin 6 DEM: Aerial Survey & DEM Dev. Methods Assessment	Basin 6 Aerial Survey & DEM Development	Basin 6 DEM Hand-over & Implementation in ATS Model		
			Implementation in model			
WIPP (Basin 6)		WIPP (Basin 6) Model: Numerical Model Assessment	ATS Basin 6 SW/GW Model Training & Development	ATS Basin 6 SW/GW Model Training & Development	ATS Model Calib./Validation	Model Implementation/ Hand-over
					Implementation in model	
WIPP (Basin 6)				WIPP (Basin 6): Field observation & data analysis	Field observation & data analysis	Hand-over

*DEM: Digital Elevation Model, SW: Surface water, GW: Groundwater

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DOE-FIU Cooperative Agreement

Upcoming Events Announcement

DOE Fellows Poster Exhibition

DOE Fellows Induction Ceremony

Thank You. Questions?