

Monday, September 16, 2024						
9:00 - 9:05 AM ET	Kick-Off /Welcoming Remarks (DOE-EM)	Rod Rimando (Acting Director, Technology Development) – DOE EM-3.2				
9:05 - 9:10 AM ET	Welcoming Remarks (DOE-LM)	Ms. Jalena Dayvault (Site Manager) – DOE LM				
9:10 - 10:10 AM ET	Project 3: Waste and D&D Engineering & Technology Development	FIU, DOE HQ, SRNL, PNNL, LBNL, INL, ANL				
10:10 - 10:25 AM ET	Project 3: Q & A					
10:25 am - 11:25 AM ET	Project 1: Chemical Process Alternatives for Radioactive Waste	FIU, DOE HQ, PNNL, WRPS, SRNL, SRS				
11:25 - 11:40 AM ET	Project 1: Q & A					
35-MIN BREAK [11:40 AM – 12:15 PM]						
12:15 - 1:15 PM ET	Project 2: Environmental Remediation Science & Technology	FIU, DOE HQ, SRNL, PNNL, ORNL, LANL, LBNL, CBFO				
1:15 - 1:30 PM ET	Project 2: Q & A					
	Thursday, September 19	, 2024				
2:30 - 3:30 PM ET	Projects 4 & 5: STEM Workforce Development and Training	FIU, DOE HQ (EM & LM), SRNL, PNNL, WIPP, SRS, ORP, LBNL, WRPS, INL, Grand Junction				
3:30 - 3:45 PM ET	Project 4 & 5: Q & A					
BREAK [3:45 – 4:00 PM]						
4:00 - 5:00 PM ET	Wrap Up (FIU Projects 1, 2, 3, 4 & 5)	FIU, DOE HQ (EM & LM)				

Advancing the research and academic mission of Florida International University



DOE-FIU Cooperative Agreement Annual Research Review – FIU Year 4

PROJECT 2 Environmental Remediation Science & Technology



Advancing the research and academic mission of Florida International University



FIU Personnel and Collaborators

Principal Investigator: Leonel Lagos

Project Manager: Yelena Katsenovich

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

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DOE-EM: Genia McKinley, Rod Rimando, Skip Chamberlain, Nick Machara, Latrincy Bates, Alexander Koenig

DOE-SRS: Stephen Stamper

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

LBNL: Haruko Wainwright (LBNL/MIT), Zexuan Xu

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

DOE-ORP: Paul Schroder

LANL: **Jonathan Icenhower, **Juliet Swanson, David Moulton, Jay Je-Hun Jang, Jean-Francois (Jef) Lucchini

DOE-CBFO: Anderson Ward

ORNL: **Eric Pierce, **Alexander Johs

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*Former contributors **Tasks on hold



Project Tasks and Scope

TASK 1: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE HANFORD SITE

- 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 2.1Investigate 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 On Hold

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

TASK 7: ENGINEERED MULTI-LAYER AMENDMENT TECHNOLOGY FOR HG REMEDIATION ON OAKRIDGE RESERVATIONOn Hold





Task 1

Remediation Research and Technical Support for the Hanford Site









Experimental Support of Lysimeter Testing



Subtask 1.4: Experimental Support of Lysimeter Testing

Site Needs:

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

Objective:



To investigate the impact of major elements, (Ca, Si, Al) present in grout-contacted solution on 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).

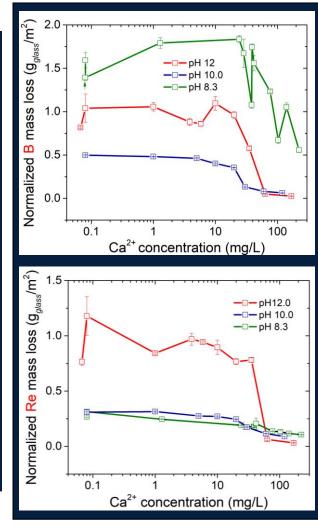


Subtask 1.4: Experimental Support of Lysimeter Testing

FIU Year 4 Research Highlights & Accomplishments:

- Investigated impact of major elements on dissolution behavior of borosilicate ORLEC28 glass
 - Product Consistency Test (PCT): Effect of Ca²⁺ on dissolution rate of glass at varying Ca²⁺ conc. (0-130 mg/L Ca²⁺) and pH (8, 10 and 12)
- PCT: Effect of Al³⁺ on dissolution rate of glass at varying temperature, Al³⁺ conc. (0-40 mg/L Al³⁺) and pH (8, 9, 10).
- XRD, BET, SEM/EDS analyses of treated glass in Ca- and Al-amended solutions.
- Publications and presentations:
 - Y. Katsenovich, V. Drozd, S. Kandel, L. Lagos, R.M. Asmussen, The corrosion behavior of borosilicate glass in the presence of cementitious waste forms. Dalton Trans. 53 (2024), 12740.
 - V. Drozd, Y. Katsenovich, L. Lagos. M. Asmussen, Borosilicate glass dissolution in the presence of cementitious waste forms (invited talk). Goldschmidt 2024, Chicago, 18-23 August 2024.

Chemical composition of a GC					
solution via ICP-OES and IC analysis					
Analyte	mg/L				
Si	6.35				
Na	28.73				
K	28.54				
Ca	132.33				
Fe	1.34				
<u>AI</u>	<u>6.75</u>				
SO ₄	31.50				
CI	1.08				
pH of the solutions					
Grout-contacted	11.5				
Sediment-	8.7				
contacted					
Grout/Sediment-	8.3				
contacted					



Normalized mass losses of B and Re by glass in PCT at 90°C at different pH in Ca-amended solution.



- Boron normalized mass loss has nonuniform trend as a function of pH.
- Speciation modeling is planned to explain the experimental observation.

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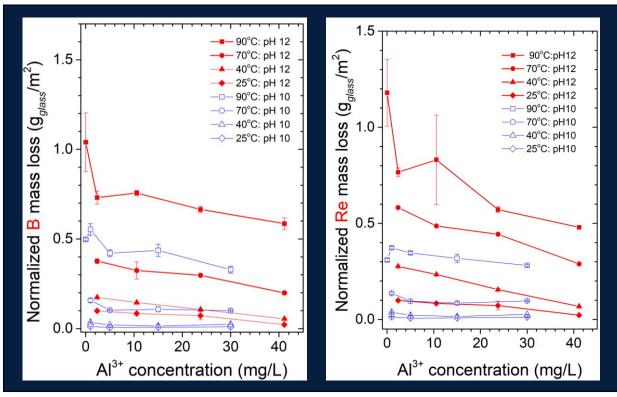


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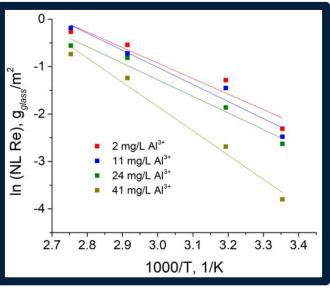
Subtask 1.4: Experimental Support of Lysimeter Testing

FIU Year 4 Research Highlights & Accomplishments:

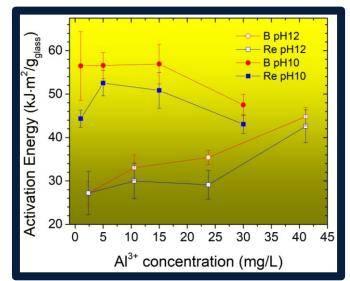


Normalized mass losses of B and Re by glass in PCT at varying temperature and pH in Al-amended solution.

- Al suppresses the dissolution of the glass
- Compared with Ca²⁺, the effect of Al³⁺ is much weaker
- Effect of aluminum is stronger at high pH
- Activation energy of glass dissolution shows weak dependence on Al concentrations at lower pH.



In (NL) vs. 1/T plots for Re loss at pH 12.



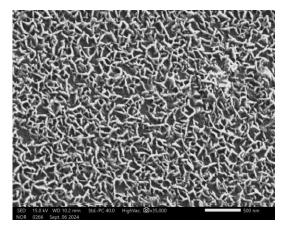
Activation energy of B and Re releases as functions of Al³⁺ concentration at pH 12 and 10.



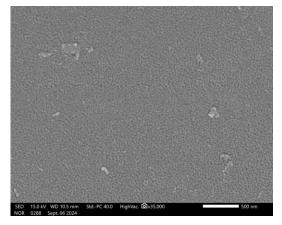
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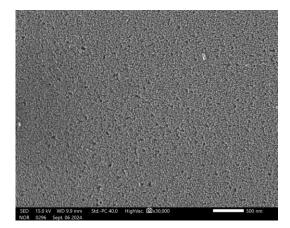
FIU Year 4 Research Highlights & Accomplishments:



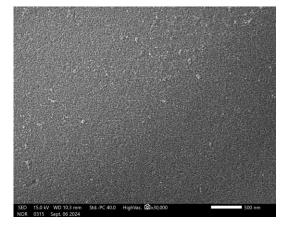
Al-amended (30 mg/L Al) pH12, 90°C



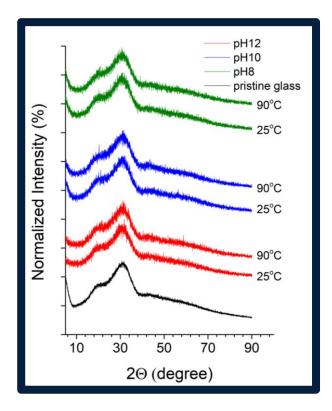
Al-amended (30 mg/L Al) pH12, 25°C



Al-amended (30 mg/L Al) pH10, 90°C



Al-amended (20 mg/L Al) pH8, 90°C



XRD patterns of glass treated in Al-amended solutions (30 mg/L Al³⁺) at different conditions of pH and temperature.

• No crystalline precipitates detected after glass treatment.

SEM images of glass particles surface after treatment in Al-amended solutions.

 Flake-like precipitates observed after treatment at pH 12 and 90°C.



Subtask 1.4: Experimental Support of Lysimeter Testing

FIU Year 5 Projected Scope

- Investigate via a series of static product consistency tests (PCTs) at variable temperatures (70°C and 90°C) the influence of various grout and geopolymer waste forms to simulate specific conditions observed in current field lysimeter experiment at PNNL.
- Support glass characterization studies via microscopy, spectroscopy, and X-ray diffraction techniques.



Element	рН 12, 90°С	рН 12, 25°С	рН 10, 90°С	рН 8, 90°С
Fe	0.28(12)	0.25(10)	0.33(6)	0.33(11)
Ca	1.11(0.23)	1.15(22)	1.12(13)	1.45(31)
K	1.93(0.25)	2.08(21)	1.98(13)	1.86(17)
Na	10.32(1.10)	11.82(1.22)	11.69(1.94)	6.32(84)
AI	3.72(23)	3.70(19)	3.90(32)	3.78(30)
Si	12.53(98)	12.69(59)	13.34(55)	13.31(99)
Mg	0.41(5)	0.40(6)	0.44(5)	0.41(7)
Ti	0.22(29)	0.14(13)	0.15(19)	0.27(32)
Zr	3.62(28)	3.59(15)	3.78(19)	3.76(29)
Sn	0.74(25)	0.75(22)	0.68(15)	0.82(19)



This work supports WRPS Field Lysimeter Test Facility and ILAW glass testing programs





Subtask 1.5

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



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

Site Needs:

- Research evaluates the re-oxidation behavior of Tc and U in the presence of nitrate (NO₃⁻) after application of strong reductants coupled with ammonia gas injections for potential vadose zone remediation.
- One limitation of strong reductants technology is these reduced forms of U(IV) and Tc(IV) may re-oxidize over time, dissolving back into the aqueous phase after reductive capacity is consumed and conditions return to natural conditions.
 - To achieve more permanent immobilization, additional strategies are being explored that involve incorporating Tc and U into other low solubility phases or coating them.
- This is the first attempt to couple strong reductants with ammonia gas treatment to prolong the effectiveness of contaminant immobilization.

Objectives:

Quantify the immobilization of Tc(VII) using a combined treatment of Tc(VII) by strong reductants such as ZVI and SMI in the presence of co-contaminants, U(VI), nitrate, followed by ammonia gas injection and investigate potential remobilization of reduced Tc(IV), U(IVI) and other targeted contaminants throughout the process.





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

FIU Year 4 Research Highlights & Accomplishments:

- Studied re-oxidation behavior of ⁹⁹Tc, U(VI), and NO₃⁻ after treatment with strong reductants:
 - $\circ\,$ 1.0 wt% (of sediment) ZVI and 1.0 wt% SMI.
 - 10 g sediment + 100 mL solution + 100 mg of ZVI or SMI in triplicate samples
 - Ringold Formation sediment <2 mm
 - PW: pH 8.2, 100 µg/L Tc, 150 mg/L U, 204 mg/L nitrate.
- Two phases of experiments:
 - Phase 1: Under anaerobic conditions for 37 days
 - Phase 2- In aerobic conditions after the addition of ammonia hydroxide for 49 days.
- Total testing = 86 days.

- Monitored changed for pH, ORP, DO, Tc, U, NO₃⁻, SO₄²⁻ concentrations at each sample point.
- 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.
- Use solids for characterization studies after the completion of reoxidation experiments.



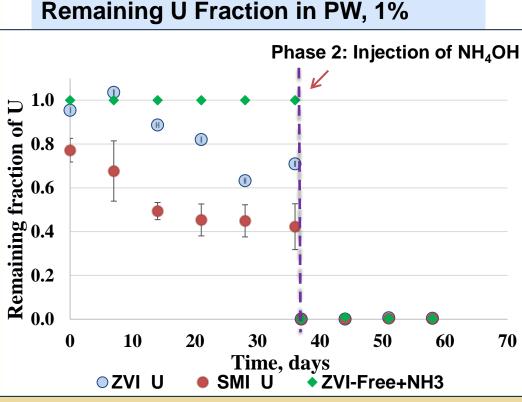


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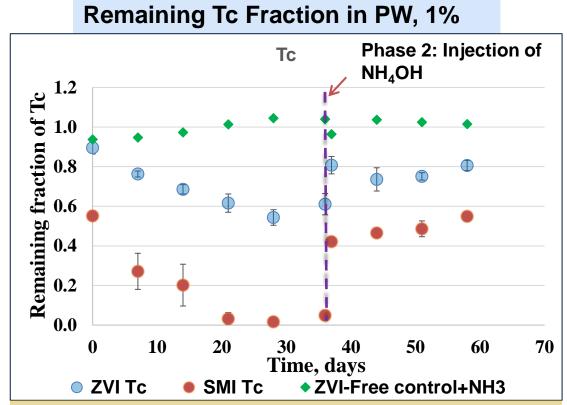
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Subtask 1.5: Remediation Research on Combination of Reduction and Sequestration Treatment (NEW)

FIU Year 4 Research Highlights & Accomplishments: Results for U and Tc



- SMI was more efficient to reduce U in the anaerobic conditions
- $\circ \quad U \text{ concentration dropped after the addition of } \\ NH_4OH \text{ in aerobic conditions, likely due to the } \\ \text{formation of U hydroxide at a pH ~11.} \\ \end{cases}$

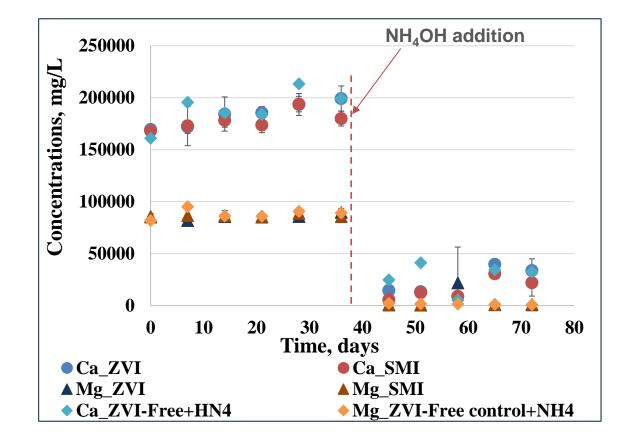


- SMI was more efficient at reducing Tc under anaerobic conditions
- The concentration of Tc rebounded after the addition of NH_4OH in aerobic conditions.
- In the reductant-free control, Tc level remained unchanged.



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

FIU Year 4 Research Highlights & Accomplishments: Changes in Ca and Mg



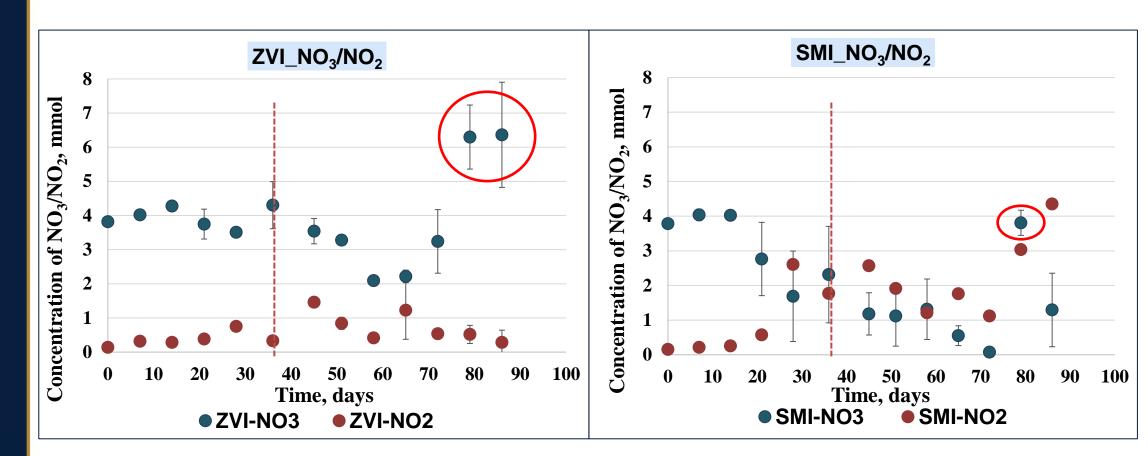


- In Phase 2, after the addition of NH_4OH , the system traps CO_2 , leading to the precipitation of $CaCO_3$ and $MgCO_3$. As a result, the aqueous concentrations of Ca and Mg significantly decrease.
- \circ The behavior of ZVI-Free control+ NH₄OH samples is identical to that of samples amended with ZVI/SMI.



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

FIU Year 4 Research Highlights & Accomplishments: Changes in NO₃/NO₂





NO₂ concentration is higher in the presence of ZVI

SMI is more effective in NO₃ removal



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

FIU Year 4 Research Highlights & Accomplishments: XRD results

Sediment:

- Quartz
- Albite
- Anorthite
- Traces of metaschoepite
- Laumonite (Ca-AI-Si)
- Cancrinite Na-Al-Si-CaCO₃
- Calcite
- MgCO₃

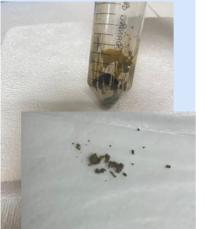


- Centrifuged and dried samples with removed sediment.
- Separated dried • precip. on top and bottom samples.

Top clay-like ppt



Bottom ppt



Top clay-like ppt:

- **Montmorillonite**
- Goethite/Lepidocr ocite
- Silicon oxide
- Aragonite- CaCO₃ ٠

Bottom ppt sample is similar in composition to sediment:

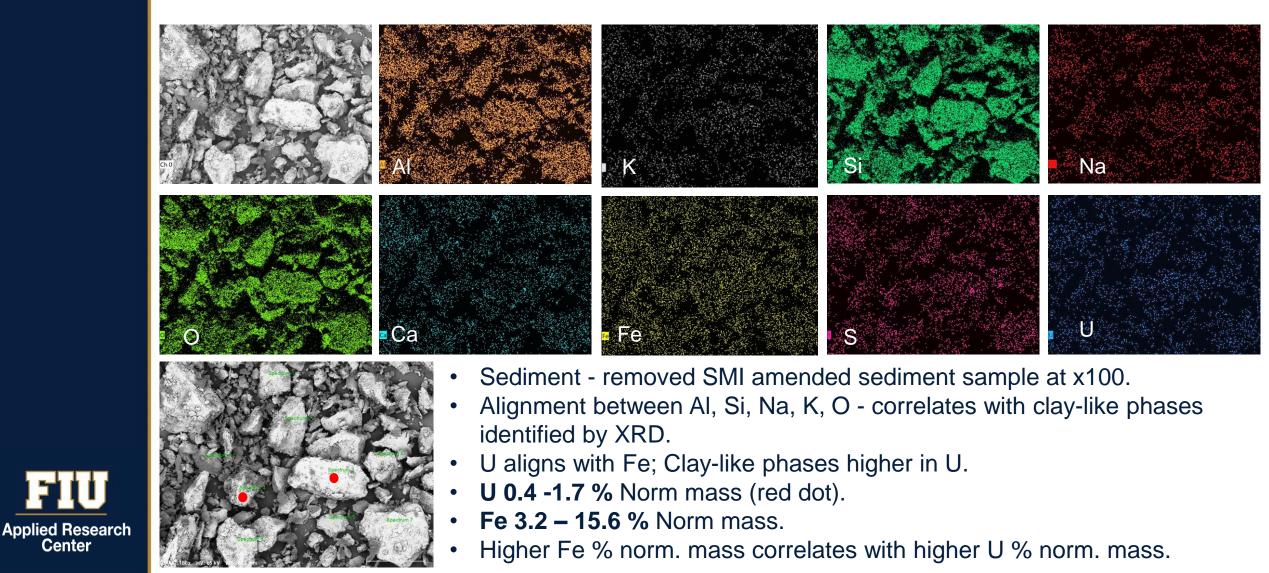
- Quartz,
- Albite
- Goethite
- Laumontite (Ca-Al-Si)
- Aragonite-CaCO₃
- Cancrinite- Na-Al-Si-CaCO₃



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

FIU Year 4 Research Highlights & Accomplishments: SMI sediment-removed ppt





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



 Undergrad student (DOE Fellow) Melissa Dieguez worked under mentorship of Dr. Alex Kugler during summer internship at PNNL, focusing on preparing column studies for cyanide scoping.



• She is now in the process of transitioning to a new position at PNNL as an Undergraduate Technical Intern – Level IV.



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FIU Year 4 Research Highlights & Accomplishments

Graduated DOE Fellow Employed by DOE





Dr. Mariah Doughman at FIU commencement ceremony (left) and with her mentor Dr. Yelena Katsenovich (right).

- Former DOE Fellow, Mariah Doughman graduated with PhD in Chemistry worked on Competitive Sorption Experiment (previous subtask under Task 1).
- Completed Graduate Fellowship during Summer 2024, sponsored by DOE-MSIPP.
- Accepted position as MSIPP-sponsored Postdoctoral Associate at PNNL.



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

FIU Year 4 Research Highlights & Accomplishments

- Oral presentation at WM2024 Symposia, "The Reoxidation Behavior of Tc(IV) and U(IV) in Perched Water of the Hanford Site Vadose Zone after Treatment with Strong Reductants"
- Submitted abstract for WM 2025 on project results, "Coupling of strong reductants with ammonia gas treatment for vadose zone remediation from commingled contaminants".

FIU Year 5 Projected Scope

- Conduct experiments that couple ZVI with ammonium hydroxide and ammonia gas treatment and investigate their effect on re-oxidation behavior of comingled Tc, U, and nitrate.
 - $_{\odot}$ Expand research conducted under anaerobic Phase 1, with pH levels 8, 9, and 10.
 - Test reduction and precipitation processes at varying pH levels.
 - \circ Duration of anaerobic Phase 1 will be extended to 3 months prior to initiating Phase 2.

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Research follows experimental matrix outlined as part of 200-DV-1 Operable Unit treatability study and supports treatment options for selected zones in Central Plateau Subsurface.



Task 2

Remediation Research and Technical Support for the Savannah River Site







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 max. contamination levels (1 pCi L⁻¹) of all radionuclides.
- F-Area wetlands have been an important sink for I-129 and other contaminants.
- Complex and diverse physical and biogeochemical processes within wetlands are mainly responsible for retaining these contaminants.
- However, these areas are sensitive to changing boundaries and geochemical conditions, resulting in release of I-129 into surrounding areas.

Objectives:



- Understand the attenuation and release mechanisms of I-129 in the aquifer and wetland sediments and the impacts of different environmental parameters
- Determine the impact of organoclays PM-199 and MRM as potential amendments.



FIU Year 4 Research Highlights & Accomplishments:

Development of Adsorption Isotherms

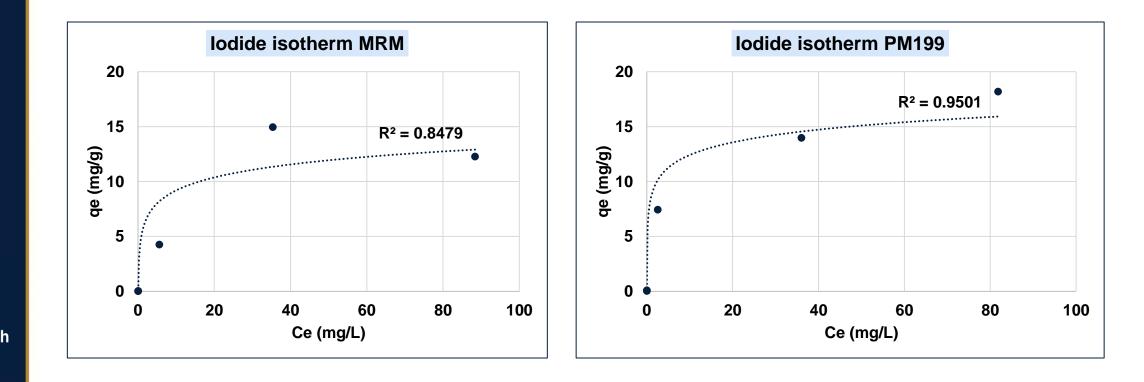
- Batch experiments were performed to determine equilibrium sorption capacities of iodide and iodate with organoclays PM-199 and MRM
 - Solid (Organoclays):Liquid = 1g/L
 - pH = 5.5
 - Equilibration time = 12 days
 - Concentration Range = 0.05 100 ppm (100 500 ppm)





FIU Year 4 Research Highlights & Accomplishments:

- Iodide sorption data indicated fast initial uptake followed by slow sorption with both MRM and PM-199.
- PM-199 has slightly higher sorption capacity than MRM with 20 mg/g and 14 mg/g respectively.





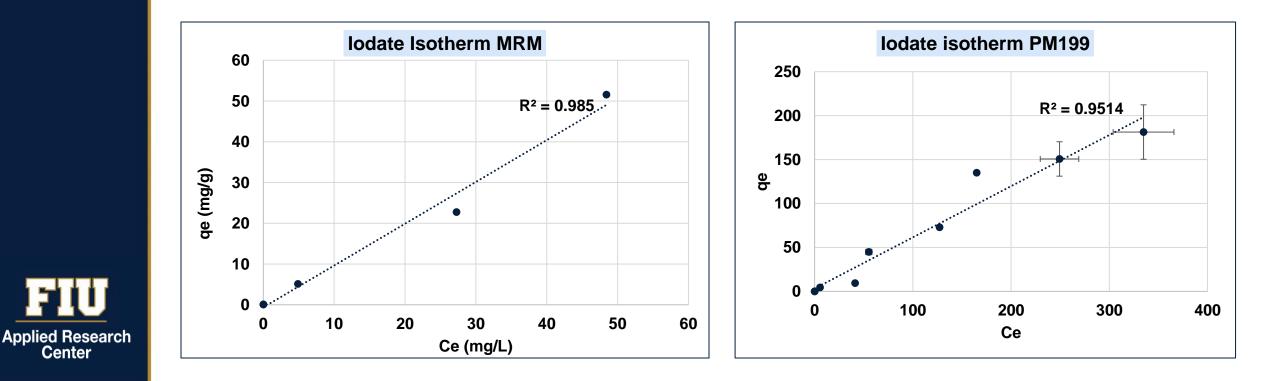


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Subtask 2.1: Environmental Factors Controlling the Attenuation and Release of Contaminants in the Wetland Sediments at Savannah River Site

FIU Year 4 Research Highlights & Accomplishments:

- lodate sorption slower compared to iodide sorption.
- Has not reached equilibrium for both MRM and PM-199.
- Extended isotherm up to 500 ppm of iodate with PM-199. Still has not reached equilibrium. ۲



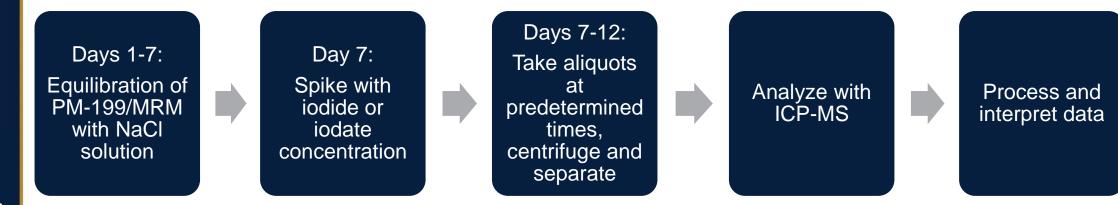


FIU Year 4 Research Highlights & Accomplishments:

Kinetics measured for iodide and iodate sorption with PM-199 and MRM in presence of SRS wetland topsoil to better understand sorption mechanism.

Procedure:

- 200 ppb iodide/iodate
- 0.1M NaCl
- 25g/L SRS wetland topsoil
- 1g/L organoclay

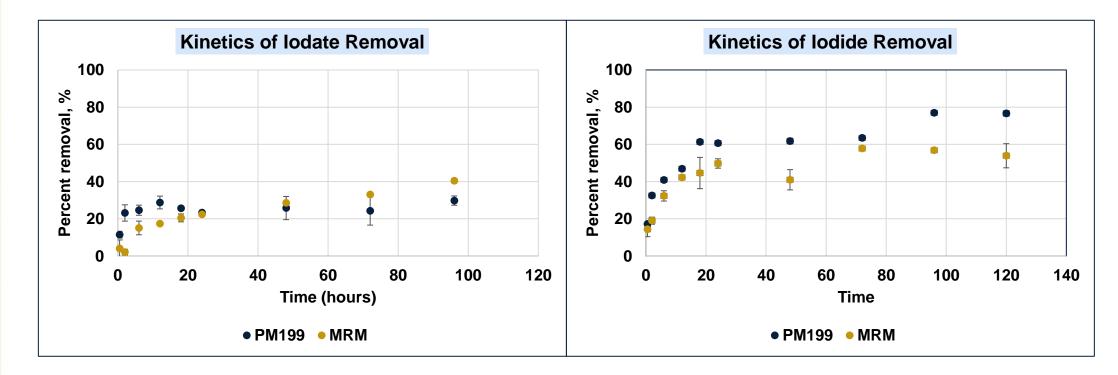


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FIU Year 4 Research Highlights & Accomplishments:

- Iodide was more effectively removed from solution than iodate.
- Initial uptake was faster for PM-199 treated samples of both iodine species.
- Initial uptake was also faster for iodide for both MRM and PM-199 treatment groups.

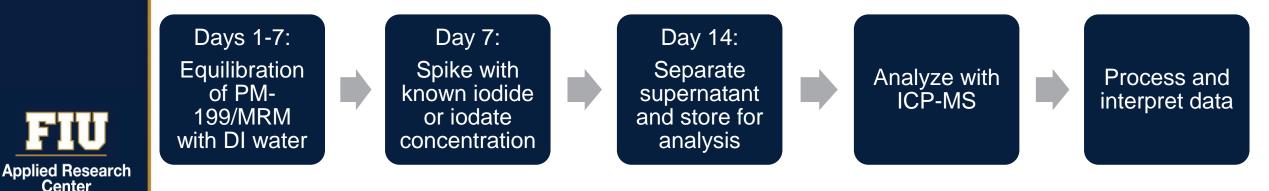


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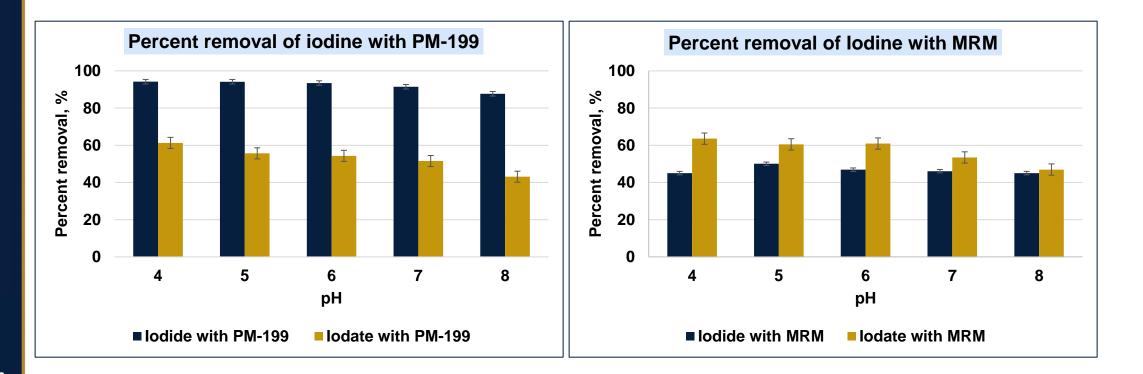
Effect of pH on iodine sorption onto wetland sediment with organoclay amendments.

- 100 ppb iodide/iodate
- 25 g/L SRS wetland topsoil
- 1 g/L organoclay
- pH range 4-8





- PM-199 was shown to be more effective at removing iodide than iodate at all pH values.
- Changing pH from 4-7 did not have a significant impact on removal capacity for both organoclays.
- A pH of 8 only slightly reduced to removal capacity when compared to the other pH values, due to the organoclays becoming negatively charged at pH >7.



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FIU Year 5 Projected Scope

- 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









Investigating the Effect of KW-30 (Humate Material) on Co-contaminant Removal



Subtask 2.2: Investigating the Effect of KW-30 (Humate Material) on Co-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.
- FIU's 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, sorption behavior of modified humic substances (KW-30) for groundwater remediation and effect of sorbed humic substances on co-contaminant (uranium and iodine) removal.





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

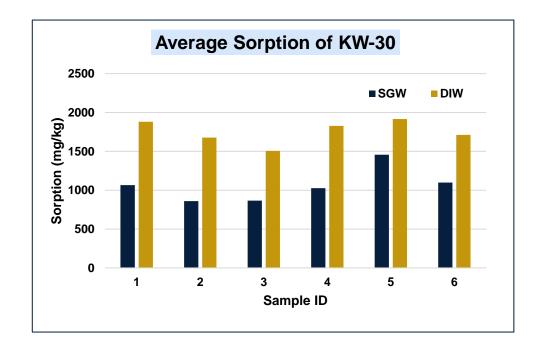
FIU Year 4 Research Highlights & Accomplishments:

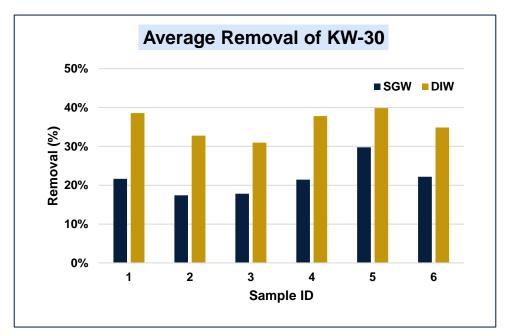
- Conducted batch experiments to study the effect of ions on humate sorption.
 - Sediment samples from FAW1 70-90 ft, sieved through a 2mm sieve
 - $\circ~$ 200 mg of dried SRS sediment
 - 50 ppm modified humic acid (KW-30)
 - 20 mL of DIW and SGW
 - o pH 4.0 (0.1 M HCI/NaOH)
 - \circ 100 rpm for 7 days
 - Centrifuged at 2700 rpm for 30 minutes
 - Supernatant was analyzed via UV-Vis spectrophotometer





- Sorption of KW-30:
 - SGW samples: 859 -1457 mg/kg (average: 1,060 mg/kg)
 - DIW samples: 1,500 1,900 mg/kg (average: 1,750 mg/kg)
- Removal % of KW-30:
 - SGW samples: 17% 29%
 - DIW samples: 32% 39%

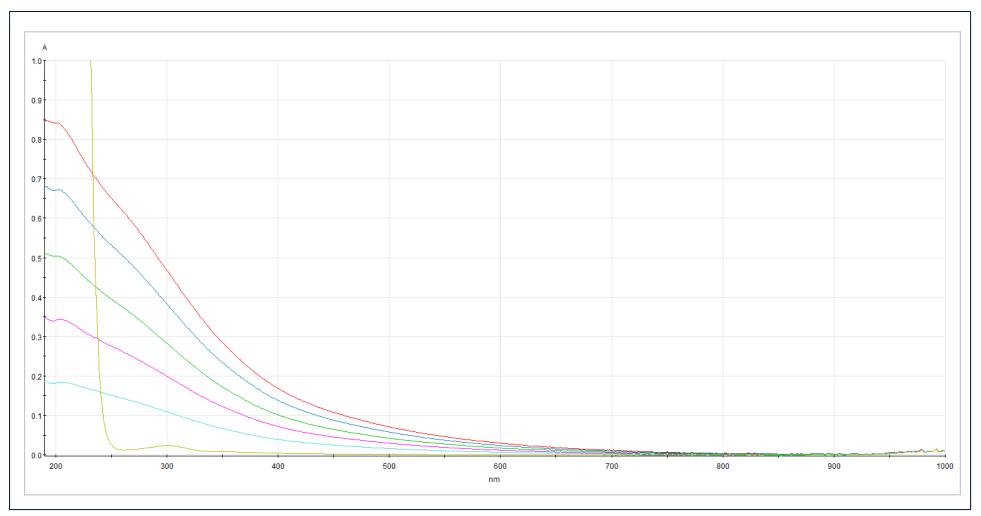






FIU Year 4 Research Highlights & Accomplishments:

• Conducted spectrum analysis of SGW and DIW calibration standards with UV-Vis.







FIU Year 4 Research Highlights & Accomplishments:

- Studied influence of humate and GW ions on kinetics of uranium removal
 - 200 mg of SRS sediment*
 - pH 4 (0.1M HCI/NaOH)
 - U & I: 700 ppb & 150 ppb
 - Perchlorate: 0.01M
 - Collected 200 µL aliquots for 2 weeks
 - Analyzed samples via ICP-MS
- Control Samples no sediment
- Uncoated Sediment Samples 200 mg of sediment with no KW-30
- Coated Sediment 200 mg of sediment coated with KW-30





FIU Year 5 Projected Scope

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





Task 3

Contaminant Fate and Transport Modeling for the Savannah River Site





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

Overall Problem:

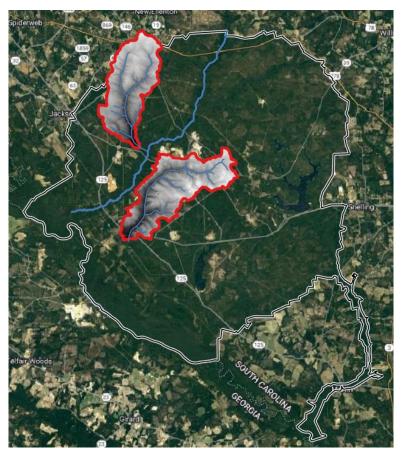
• SRS & other DOE sites challenged with heavy metal & radionuclide surface & subsurface contamination.

Site Needs:

• Evaluate impact of extreme hydrological events & long-term hydrological changes on GW-SW interactions, as these influence the fate and transport of major contaminants of concern in SRS streams.

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 numerical models to evaluate impact of extreme hydrological events & long-term hydrological changes on GW-SW interactions, and fate & transport of major contaminants in SRS streams.
- Establish long-term monitoring strategy.
- Collect field data to support model calibration & validation.
- Train FIU grad. & undergrad. students (DOE Fellows).

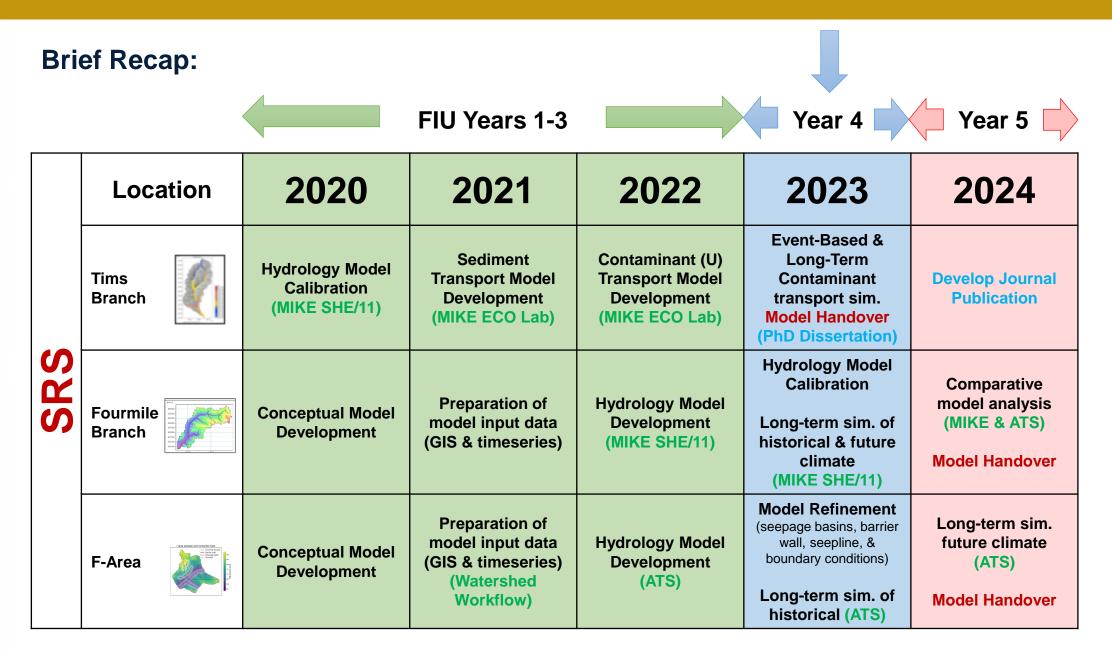


Tims Branch & Fourmile Branch watersheds at SRS.





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



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Calibration of the Tims Branch Watershed Model and Scenario Analysis



FIU Year 4 Research Accomplishments:

Objectives for FIU Year 4:

- Complete simulations and evaluation of event-based uranium (U) transport in Tims Branch (TB) watershed (Milestone 2023-P2-M7).
- Complete draft manuscript on U transport model for TB (Milestone 2023-P2-M13).
- Complete long-term simulations to evaluate hydrological response of TB due to climate change and impact on U transport.

Accomplishments:

- Completed event-based simulations of U transport in TB.
 - Former DOE Fellow, Juan Morales, graduated with PhD in Env. Health Sciences in March 2024 – Part of dissertation based on this research. Also, recipient of Dean's Award for Academic Excellence. Joined Marine Corps in 2022.
- MIKE licensing issue while attempting to upgrade software to perform long-term simulations of U transport in TB » 6-mth delay.
- Currently adjusting input parameters and running simulations to achieve better results and identify best MIKE ECO Lab model parameters to simulate U transport within river network of TB.

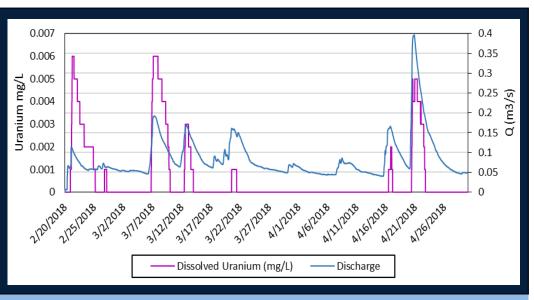






FIU Year 4 Research Accomplishments: Event-Based U Transport in Tims Branch Watershed

- Sensitivity analysis to determine controlling variables and optimum values of parameters affecting U geochemical processes in TB.
- *Koc* and *foc* identified as controlling variables primary focus of model calibration process.
- Simulation results highlight Koc to be driver of U flux at TB outlet, thus optimum Koc values determined.
- Simulated U flux in alignment with observed data in published literature (Hayes 1986).
- Next step: Obtain accurate stream flow data and run model for short period.
 - Data derived from earlier experiment in 2018. •
 - **Breakthrough curves** simulated, representing • dissolved U concentration in TB outlet.



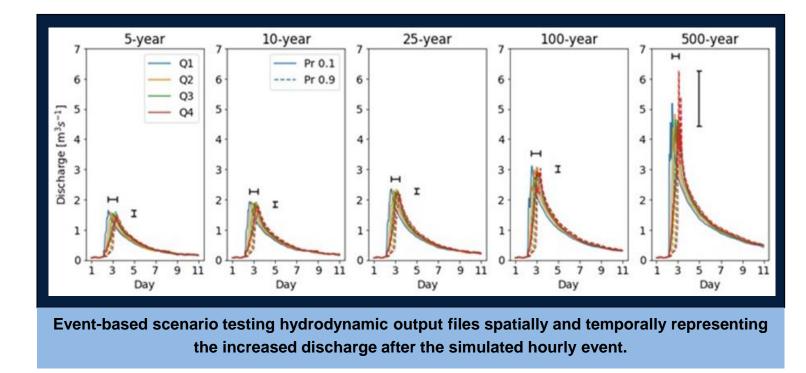
Simulated breakthrough curves of dissolved U and discharge in response to increased discharge scenarios caused by episodic precipitation in TB outlet for the evaluation calibration period.

> (Koc) – organic carbon partition coefficient (foc) – fraction of organic carbon





FIU Year 4 Research Accomplishments: Event-Based U Transport in Tims Branch Watershed



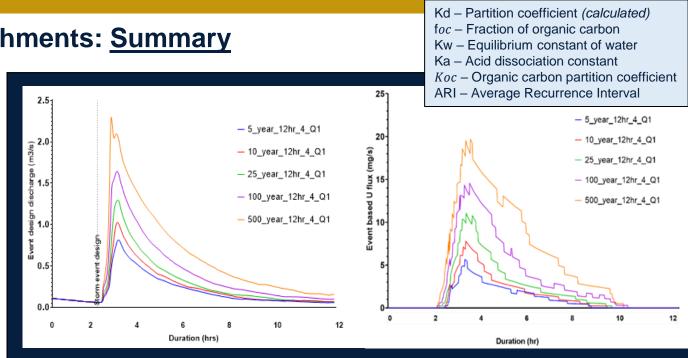
- Tested U transport scenarios once satisfactory model performance achieved from calibration of MIKE HD, AD, and ECO Lab modules.
- Design events calibration: 2/20/2018 4/30/2018.
- Successfully generated 1-D hydrodynamic model and ECO Lab files highlighting 6 design storm events (5-yr, 10-yr, 25-yr, 50-yr, 100-yr, and 500-yr).





FIU Year 4 Research Accomplishments: Summary

- CT model calibrated with data from literature, historical observed and calculated inputs.
- Enabled estimation of particulate & dissolved U phases in sediment & water column. Numerically validated against observed data.
- Calibration of U transport determined *Koc* is significant in U desorption and adsorption.
- Other governing factors in U resuspension include Kd, foc, Kw, Ka and Koc for which literature and field observations used.
- Model capable of simulating U transport for different extreme storm event scenarios.
- Computed findings help in understanding U transport during extreme events.



Event-based scenario results:

(1) increased discharge after episodic storm events (left)(2) U flux due to increased precipitation and discharge at Tims Branch outlet (right).

- Greatest quantity of U-sorbed sediment transported in 500-yr ARI peak discharge.
- Considerably more U transported in 500-yr ARI (3,550% increase at TB outlet), (1,327% increase in Steed Pond) when compared to base flow U measurements.
- These estimations can be used to support site-specific environmental assessment, planning, and decision-making for TB watershed at SRS.





FIU Year 4 Projected Scope

- Complete long-term simulations for various climate change scenarios and evaluate the long-term hydrological response in Tims Branch and its impact on U transport.
- Model handover / further implementation for additional scenarios.
- Initiate draft manuscript for submission in peer reviewed journal (Milestone 2023-P2-M13).

FIU Year 5 Proposed Scope

• Complete manuscript for submission in peer reviewed journal.









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

(Fourmile Branch MIKE Model)



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

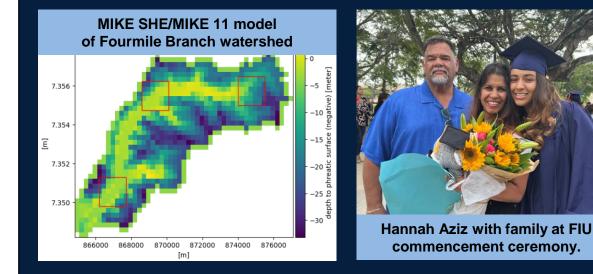
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FIU Year 4 Research Accomplishments:

Objectives for FIU Year 4:

- Finalize calibration of Fourmile Branch (FMB) MIKE model using upstream observations (Milestone 2023-P2-M4).
- Complete long-term simulations for current & future climate (2023-P2-M10).
- Generate report (Deliverable 2023-P2-D5).

Accomplishments:



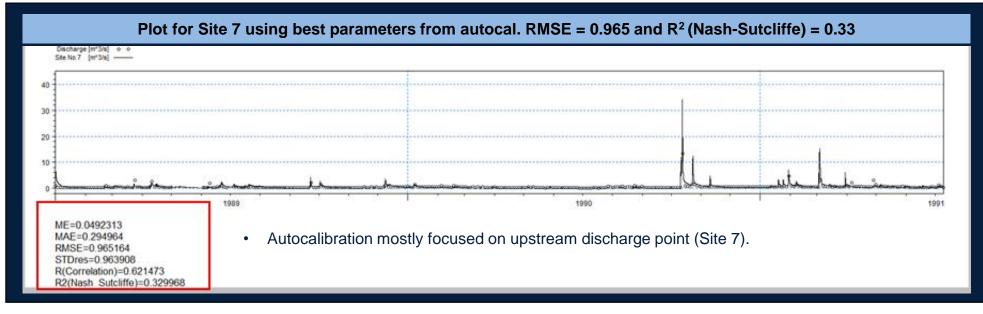
- Completed MIKE Autocalibration of FMB model using upstream observations.
- Downloaded climate forcing from NASA climate model and converted to compatible MIKE format.
- Benefits of **NEX-GDDP-CMIP6** dataset vs. original CMIP modeling archive:
 - Downscaled product of daily simulated values for 8 atmospheric variables (e.g., precip, temp, humidity, wind) •
 - Bias corrected & spatially disaggregated using monthly historical observations to 1/4-deg. horiz. resolution.
- Initiated long-term hydrology simulations using historical data & climate model projections.
 - 4 different climate scenarios represent climate extremes (wet spells & atmospheric drought) & their impact on occurrence of hydrological (discharge & groundwater) extremes.
- DOE Fellow, Hannah Aziz graduated with BS in Env. Engineering in Spring 2024 & accepted to PhD program at Northwestern University in Fall 2024.



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

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FIU Year 4 Research Accomplishments: MIKE Fourmile Branch Model Autocalibration



- FY23 1st Qtr → set up MIKE FMB watershed model autocal process focusing on parameters for which no estimates avail. from public datasets:
 (subsurface conductivity; storage values of upper 2 aquifer systems; friction parameter of river network)
- Thompson et al. (2004) provided basis for using higher resolution model to better define SW/GW interaction using 3-4 parameters with shorter evaluation time periods.
- MIKE-11 results initially saved every 15 mins to match Site 7 observed 15-min data which significantly improved results; Due to long run times & large files occupying significant disk space, results saved every 24 hrs.
- Similarly, MIKE-11 SZ and UZ timeseries were configured to save every 24 hours.





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Climate Forcing for Long-Term Model Simulations

4 climate scenarios considered for long-term simulations and impact on discharge:

- SSP1-2.6: Sustainability (Taking the Green Road) 1.8°C
- SSP2-4.5: Middle of the Road 2.7°C
- SSP3-7.0: Regional Rivalry (A Rocky Road) 3.6 °C
- SSP5-8.5: Fossil-Fueled Development (Taking the Highway) 4.4 °C

Different projections for future GHG emissions & temp variability.

MIKE model setup:

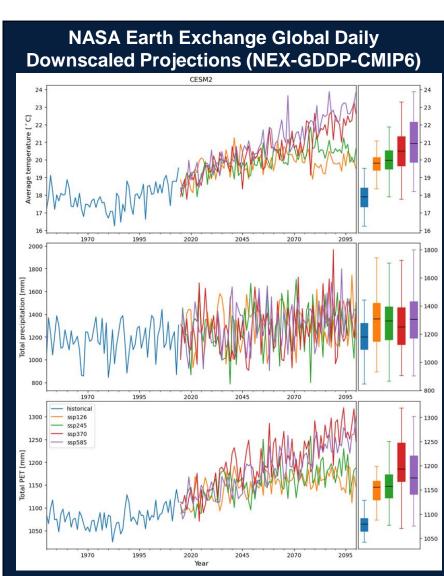
Python script developed to automate CMIP6 download and conversion to MIKE readable format.

- Historical simulations: 1950-2015
- Future simulations: 2015-2100

ATS model setup:

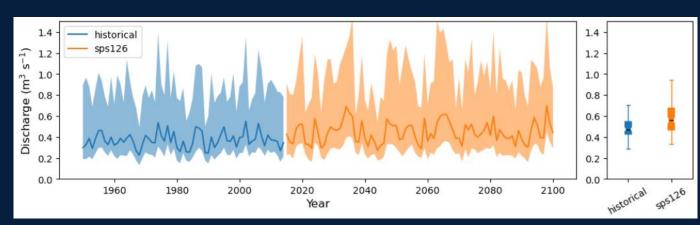
- Python package, Watershed Workflow, extended to automate CMIP6 download and conversion to ATS readable format.
- ATS model simulations time consuming, so focus on 5 periods:
- Historical simulations:
 - 1957-1970
 - 1987-2000

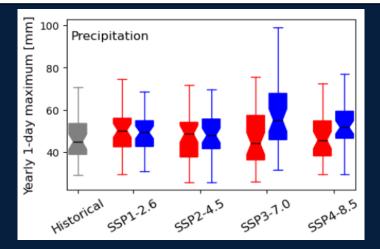
- Future simulations:
 - 2017-2030
 - 2047-2060
 - 2077-2090



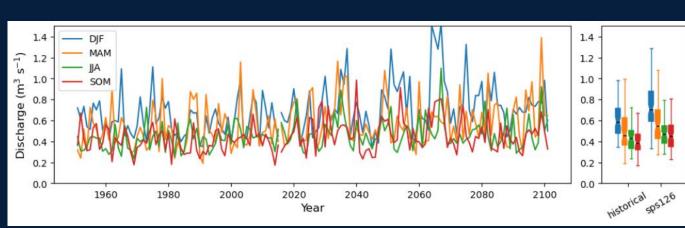


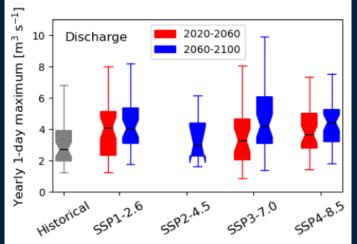
Long term changes in discharge





Performed long-term simulations MIKE





Changes in average discharge dynamics

How climate change impacts extremes



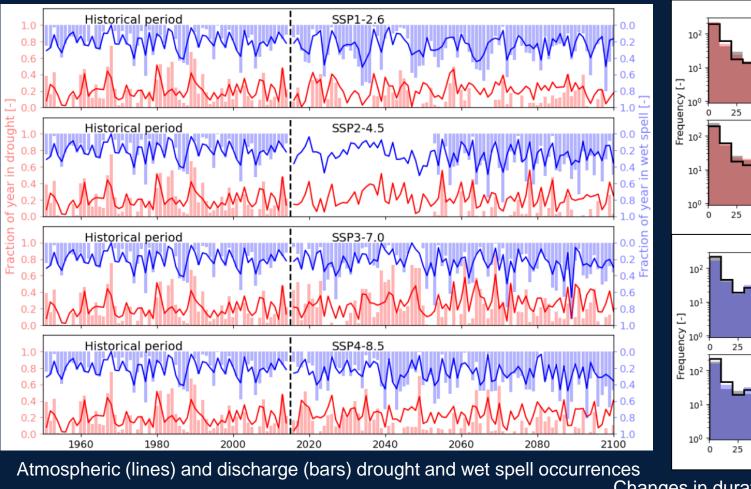
- For all climate scenarios an increase in average discharge is observed, occurring over all 4 seasons.
- Yearly maximum precipitation and discharge events overall slightly increase, with biggest shift of SSP3 for period 2060-2100.

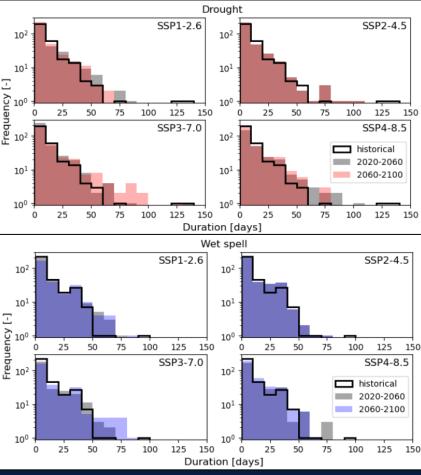


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Long term changes in climate extremes





Changes in duration distributions of atmospheric extremes

- All climate scenarios result in increased wet spell occurrences throughout the year for future simulations.
- Occurrence of drought more variable between models, decreasing for SSP1, more regular and longer for SSP-3.7, increasing for SSP4 until 2050, decreasing in occurrence afterwards.
- For SSP3 and SSP4, duration of longest drought periods increase, for SSP3 this also holds for duration of long-term wet spell.





Subtask 3.2

Model Development for Fourmile Branch with Specific Focus on the F-Area Wetlands (F-Area ATS Model)



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

FIU Year 4 Research Accomplishments: F-Area ATS Model

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Ē −1.0 v −1.5

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.

Accomplishments:

- Refined ATS model of F-Area hillslope domain to include upstream channel flow by applying Neumann boundary condition at inflow points (2023-P2-M2).
- Extracted simulation data from MIKE FMB model to use in ATS F-Area model for upstream boundary conditions.

Fourmile Branch Groundwater Along Transect Barrier wall Seepage basin MIKE North Inflow Seep Line Transect 5 0.010 **MIKE East Inflow** Outlet Flux 35000 -20000 -Mundummunallule ATS Result Outflow

Simulations in Progress:

- Multi-year simulations of F-Area hillslope using ATS for current and future climate (2023-P2-M11).
- Report on model long-term simulations of hydrological response of F-Area hillslope (2023-P2-D5).



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

FIU Year 4 Projected Scope

Fourmile Branch MIKE Model:

- Finalize long-term simulation analysis for Fourmile Branch MIKE model for 4 climate scenarios.
- Analyze long-term changes in: (1) Actual evapotranspiration and (2) Groundwater variability
- Compare different components of the water balance.

F-Area ATS Model:

- Perform historical simulations with upstream river network boundary conditions implemented with results from MIKE model 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 5 Projected Scope

Fourmile Branch MIKE Model:

- Perform a comparative analysis of FIU's FMB MIKE model vs FMB ATS model (generated by visiting fellow from S. Korea at MIT)
 F-Area ATS Model:
- Perform simulations of F-Area hillslope using ATS for additional climate model scenarios.
- Report on model long-term simulations of hydrological response of F-Area hillslope.





Task 6

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

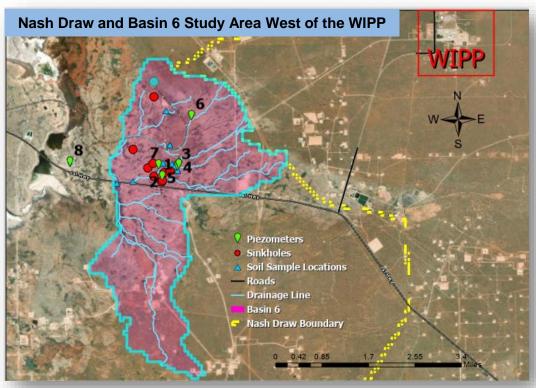




Task 6: Hydrology Modeling of Basin 6 of the Nash Draw Near the WIPP

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 occur.



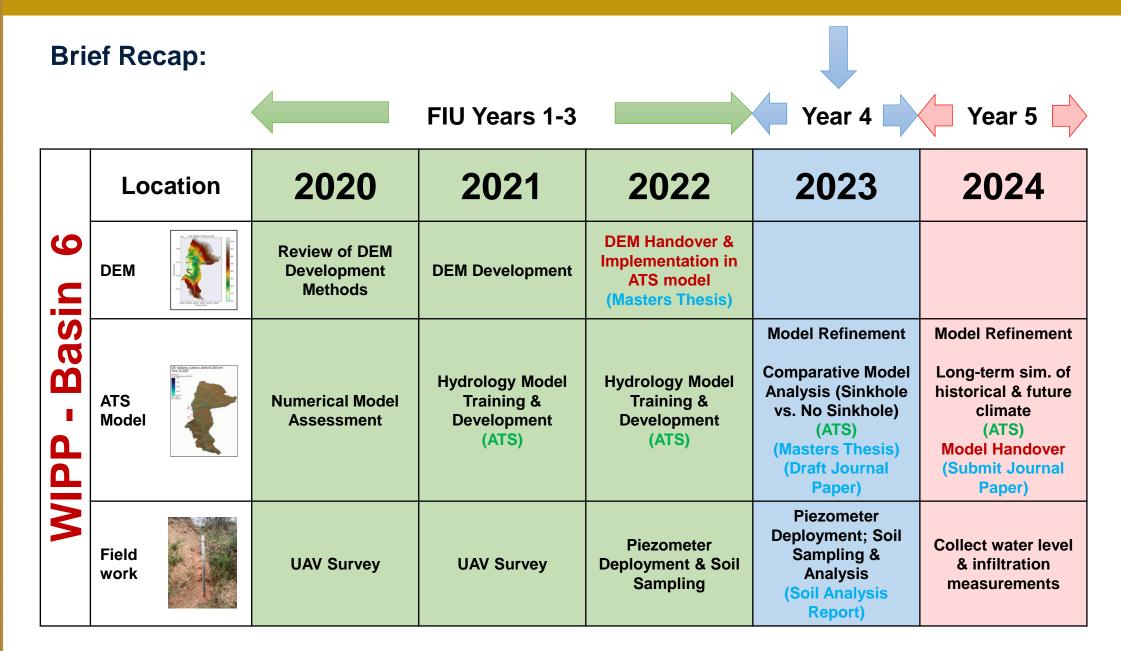
Overall Objectives:

- 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:
 - Evaluate impact of climate change and surface features (e.g., sinkholes and swallets), soil properties, and vegetation on GW recharge.
 - 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.
- Subtask 6.3: Collect field data to support model calibration and validation.





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



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Subtask 6.2

Develop a hydrological model of Basin 6 using ATS



Subtask 6.2: Develop a hydrological model of Basin 6 using ATS

FIU Year 4 Research Accomplishments:

Objectives for FIU Year 4:

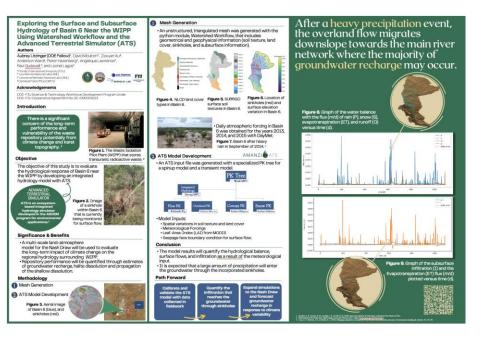
- Enhance ATS Basin 6 model to include known sinkhole locations (Milestone 2023-P2-M3).
- Complete long-term simulations of Basin 6 explicitly representing sinkholes and river network infiltration variations (Milestone 2023-P2-M8).
- Draft manuscript on multi-year simulations of Basin 6 using ATS focusing on the role of sinkholes and the river network on local and regional scale groundwater recharge (Deliverable 2023-P2-D6).

Accomplishments:

- DOE Fellow, Aubrey Litzinger, presented student poster at WM24.
- Hired new undergrad DOE Fellow, Ellie Risher, to continue supporting Basin 6 ATS modeling and field work.
- Professional abstract to WM2025 accepted for oral presentation:
 - "Simulating Hydrology and Climate Impacts on Groundwater Recharge in Basin 6 near the WIPP with the Advanced Terrestrial Simulator (ATS)".
- DOE Fellow, Aubrey Litzinger, completed draft thesis and will defend in Fall 2024.
 - "Assessing the Impacts of Weather Patterns on Surface-subsurface Hydrological Interactions in Southeastern New Mexico: A Case Study of the Nash Draw Near the WIPP Region Using the Simulator ATS".



DOE Fellow, Aubrey Litzinger, won the Roy G. Post Foundation Scholarship and presented a student poster on this research at WM2024.

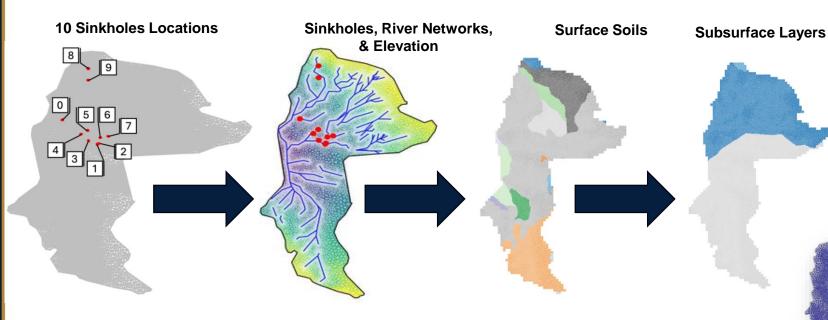






Subtask 6.2: Model Development

FIU Year 4 Research Accomplishments:



Mesh Facts:

- 69,112 triangles
- 60-meter depth
- 13 surface soils
- 4 subsurface layers
- 1 land cover type

- Used Python package, Watershed Workflow, to generate new and improved mesh.
 - Added 10 sinkholes each with radius to 20 m & depth to 10 m.
 - Increased mesh resolution, specifically around features of interest, e.g., river network & sinkholes.

Final Mesh with Sinkholes Incorporated





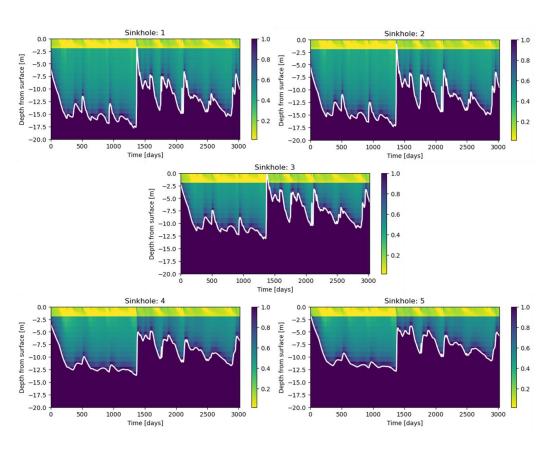
Subtask 6.2: Model Development

FIU Year 4 Research Accomplishments:

- Developed 2 integrated hydrology ATS models of Basin 6 to investigate impact of sinkholes on regional hydrology: 'Sinkholes' & 'No Sinkholes'
- Developed advanced Python script to extract specific data from ATS for in-depth analysis which will be used for all future ATS modeling work.
- Simulated 7 yrs of historical data (2012 2018). Determined sinkholes have impact on surface water & shallow subsurface water content in Basin 6.

Simulation results indicate:

- Groundwater (GW) dynamics in Basin 6 heavily influenced by location & characteristics of individual sinkholes and extreme precipitation events.
- Sinkholes reduce runoff and increase infiltration & ET for average and extreme precipitation events.
- While sinkholes have a localized impact on groundwater levels, their influence on the overall basin-wide GW table is limited.
- Similar to historical well data near WIPP, simulation results indicate that after an extreme precipitation event, the groundwater table remains elevated for months to years before gradually returning to natural levels.



Temporal variation of groundwater table (white line) and soil water content (color map) across different depths (meters) for sinkholes S1, S2, S3, S4, and S5 over time (days).





Subtask 6.2: Model Development

FIU Year 5 Projected Scope

- Refine the ATS model of Basin 6 by extending the subsurface domain to include deeper layers and allow regional GW flow across the model boundary.
- Calibrate model and perform hydrology simulations (event-based & long-term) in Basin 6 using ATS and field observations obtained in FIU Years 3 & 4 as part of Subtask 6.3.
- Perform scenario analyses with sinkhole implementation & incorporation of field data.







Subtask 6.3

Fieldwork and Data Collection to Support Hydrological Model Calibration and Validation



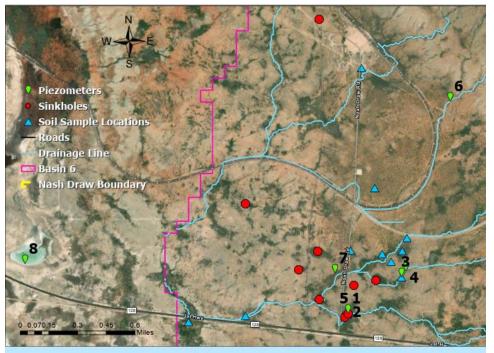
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Subtask 6.3: Fieldwork and Data Collection to Support Hydrological Model Calibration and Validation

Research Objectives:

Background:

- In-situ observations of soil texture, organic content, 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.



Basin 6 Field Sampling Locations

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.
- Use soil texture observations to evaluate quality of large-scale publicly available soil texture datasets (STATSGO2, SSURGO and SoilGrids).



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

FIU Year 4 Research Accomplishments:

Fieldwork (Summer 2024: May 31 – June 3, 2024)

- Collected water level measurements from 5 HOBO U20L pressure transducers installed in Basin 6 in Summer 2023 and performed routine maintenance.
- Deployed 3 additional HOBO units in areas of probable surface flow.
- Collected 32 additional soil samples 0-10 ft bgs in Summer 2024 to obtain soil data over broader geographic range.

Laboratory Analysis

- Analyzed 48 soil samples from Summer 2023 & completed Soil Analysis Report (Deliverable 2023-P2-D2).
- Currently analyzing soil samples collected Summer 2024.

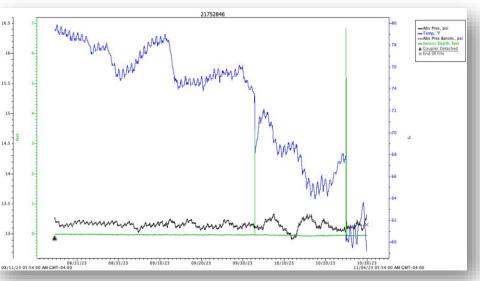
*Fieldwork support:

- Dr. Anderson Ward (CBFO)
- Dr. Dennis Powers (Consulting Geologist & subject matter specialist on Nash Draw hydrogeology)





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



Data from HOBO data logger showing variation in Temperature & Pressure

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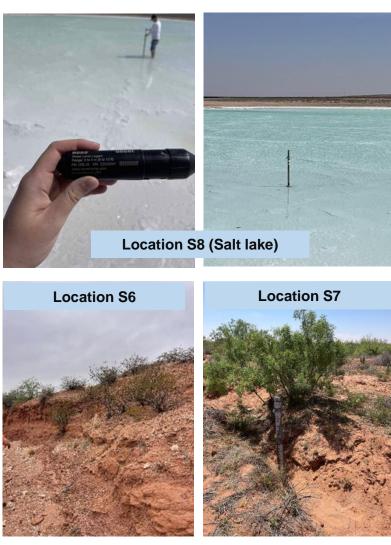


Subtask 6.3: Fieldwork and Data Collection to Support Hydrological **Model Calibration and Validation**

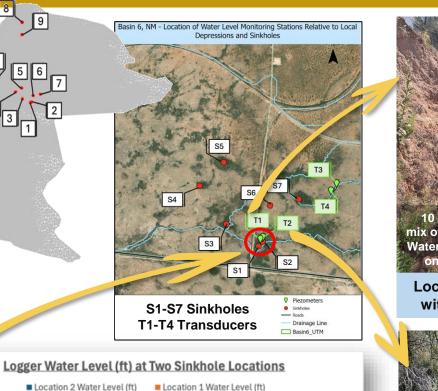
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FIU Year 4 Research Accomplishments:

Transducer Deployment



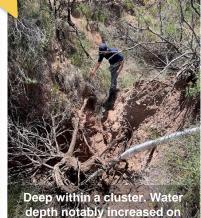
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2 significant rainfall events in 2023 from SNL-16: Oct. 2 (1.34 in/day) & Oct. 24 (1.74 in/day) Water level notably increased in S1 & S2.



10 x 16 ft sinkhole cluster mix of white, red, & gravel soil. Water depth notably increased on October 2 & 24, 2023. Location S1 (Sinkhole) with Transducer (T1)



October 24, 2023

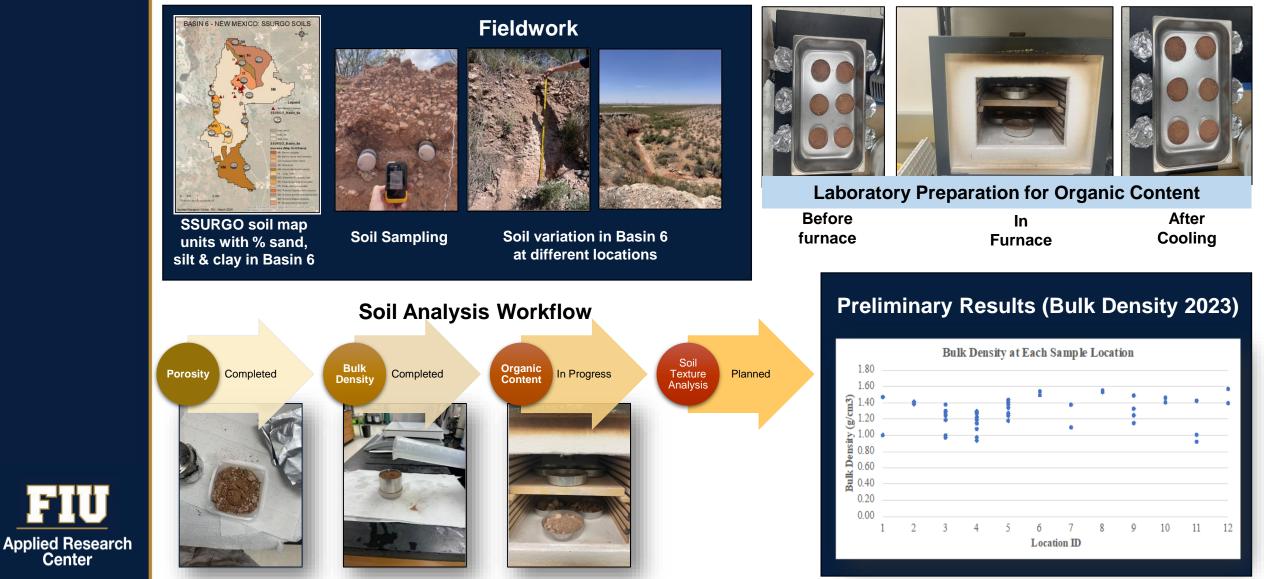
Location S2 (Sinkhole) with Transducer (T2)



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Subtask 6.3: Fieldwork and Data Collection to Support Hydrological **Model Calibration and Validation**

Soil Sampling & Analysis





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

FIU Year 4 Projected Scope

• Complete soil analysis & comparison of soil texture data with national databases (STATSGO, SSURGO, SoilGrids).

FIU Year 5 Projected Scope

- Collect water level measurements from existing sites where deployed.
- Collect infiltrometer measurements in Basin 6 along main river network and within sinkholes.
- Collect and analyze additional soil samples at different locations throughout Basin 6.





FIU Year 3 Overall Accomplishments

Highlights

Conference papers & oral presentations:

WM24

- Student Track (DOE Fellows) 1 poster by Hannah Aziz.
- Roy G. Post Scholarship Winners Session 1 poster by DOE Fellow Aubrey Litzinger.
- Professional Track 2 oral presentations by Yelena Katsenovich and Pieter Hazenberg.

Goldschmidt 2024 (Invited Talk)

• Oral presentation by Vadym Drozd, "Borosilicate glass dissolution in the presence of cementitious waste forms", Chicago, 18-23 August 2024.

Peer review publications:

- In preparation for submission to a Journal TBD: Litzinger, A., Gutierrez-Zuniga, G., Risher, E., Moulton, D., Zhang, Y., Xu, Z., Ward, A., Lawrence, A., Lagos, L., Hazenberg, P. (2024) The Role of Sinkholes and the River Network on Local and Regional Scale Groundwater Recharge in Basin 6, Using Amanzi-ATS.
- 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.
- Doughman, M., Katsenovich, Y, O'Shea, K, Hilary P. Emerson, H. P., Szecsody J, Kenneth Carroll, K, and N. Qafoku, 2024, Impact of Chromium (VI) as a Co-Contaminant on the Sorption and Co-Precipitation of Uranium (VI) in Sediments Under Mildly Alkaline Oxic Conditions, *Journal of Environmental Management*, 349, 119463
- Katsenovich, Y, Drozd, V, Shambhu Kandel, S, Lagos, L, and M. Asmussen, 2024. The corrosion behavior of borosilicate glass in the presence of cementitious waste forms, *Dalton Transactions*, 53, 12740
- Dickson, J., Estrada, C., Katsenovich, Y., Lagos, L., Johs, A., and E. Pierce, 2024. Sorption Kinetics and Stability of Conventional Adsorbents for Mercury Remediation. *Journal of Environmental Chemical Engineering*





DOE-FIU Cooperative Agreement

Upcoming Events Announcement







IBTH ANNUAL DOE FELLOWS POSTER EXHIBITION

NOVEMBER 12, 2024 1:00 - 4:00 PM FIU ENGINEERING CENTER PANTHER PIT



fellows.fiu.edu



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SAVE-THE-DATE

18th Annual DOE Fellows Induction Ceremony

WEDNESDAY NOV.

13

2024 AT 12:00 PM

2024

FIU MODESTO MAIDIQUE CAMPUS Graham Center (GC) Ballroom GC Parking, 10955 SW 15th St, Miami, FL 33199

A collaboration between the U.S. Department of Energy's Office of Environmental Management and Florida International University's Applied Research Center



Thank You. Questions?