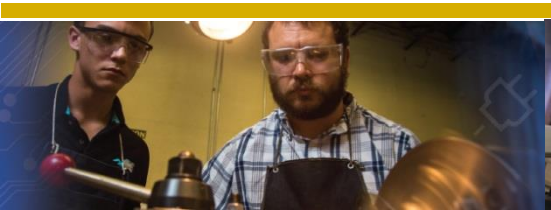
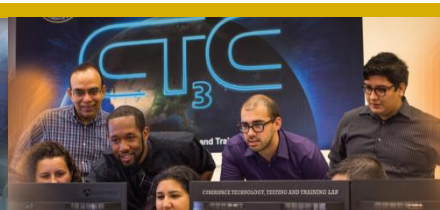
FIU PROJECT 2:
YELENA KATSENOVICH

ENVIRONMENTAL REMEDIATION SCIENCE & TECHNOLOGY

FLORIDA INTERNATIONAL UNIVERSITY





FIU Personnel and Collaborators

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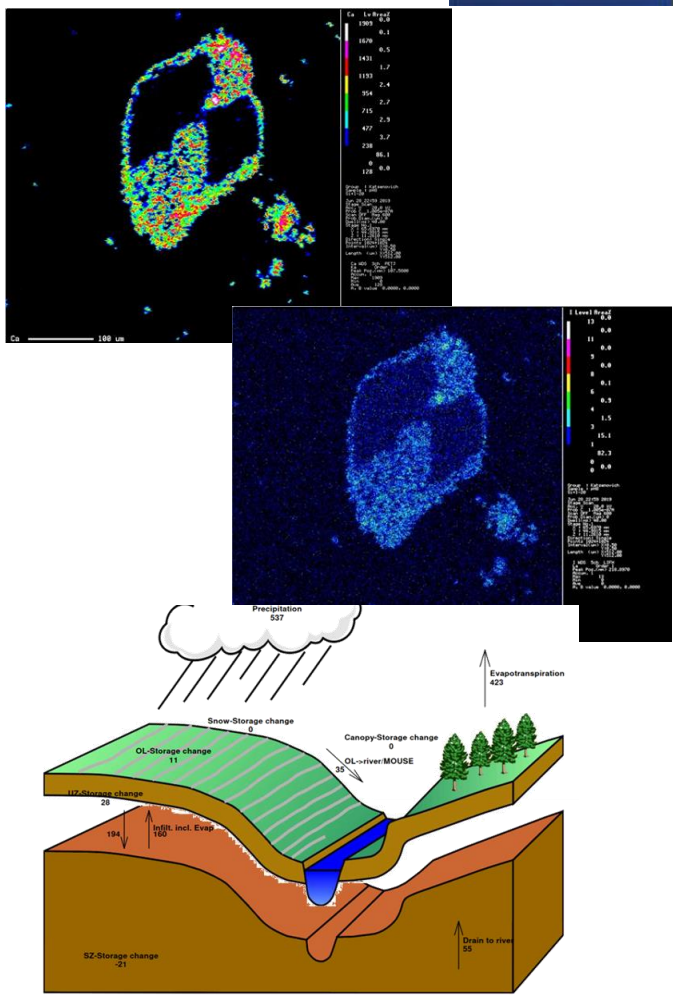
Project 2: Soil & Groundwater Research

FIU Applied Research Center

Focus on high profile EM mission to complete the safe cleanup of the environmental legacy from nuclear weapons development and nuclear energy research.

- Evaluation of new cleanup technologies, treatment and disposal options at the Hanford, SRS, and WIPP sites
  - Reduce contamination concentrations and plume size thus shrinking the extent of radiological and chemical contamination in groundwater at DOE sites.
  - Provide an integrated solution for better understanding of the mobility and fate of contaminants in soil, surface water and groundwater at DOE sites via conventional hydrologic and remediation analytical tools.



Project Tasks and Scope

TASK 1: REMEDIATION RESEARCH AND TECHNICAL SUPPORT FOR THE HANFORD SITE	
Subtask 1.1	Remediation Research of Ammonia Gas for Uranium Treatment
Subtask 1.2	Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants **(NEW)**
Subtask 1.3	Eval. of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments **(NEW)**
Subtask 1.4	Experimental Support of Lysimeter Testing
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 Sediments **(NEW)**
Subtask 2.2	Humic Acid Batch Sorption Experiments with SRS Soil
TASK 3: CONTAMINANT FATE AND TRANSPORT MODELING IN THE TIMS BRANCH WATERSHED	
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 FOR WIPP	
Subtask 6.1	Digital Elevation Model and Hydrologic Network
Subtask 6.2	Model Development

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

FIU Applied Research Center

Site Needs:

- To understand biogeochemical processes influencing behavior & fate of U(VI), Tc-99, Cr(VI), I-129 in Hanford Site's deep vadose zone (VZ) that can impact groundwater (GW).
- Research to address environmental risks and remediation challenges involving Tc-99 is high-priority activity (*Technetium Management Program Plan (DOE EM, 2016*))
- Alkaline pH manipulation is potential remediation technology that can lead to incorporation of U(VI) into sediments. Once active remediation completed, transition to MNA needed.
- Research also supports Field Lysimeter Test Facility by generating data on corrosion of various waste forms to confirm ability of lab data to model dissolution behavior in field environment.

FIU Year 10 Objectives:

- Identify physicochemical mechanisms controlling U immobilization via $NH_3(g)$ injection in Hanford VZ.
- Provide insights on stability of immobilized Tc-99 after sequestration with strong reductants.
- Evaluate attenuation processes that affect fate & transport mechanisms of contaminants of concern present in VZ sediment from Hanford Site.
- Investigate effect of grout-contacted GW on glass dissolution behavior at temperature (25°C, 40°C, 70°C) using single-pass flow-through (SPFT).

Present (FIU Year 10) Subtasks:

- **1.1** Determine long-term stability of U-solid phases after $NH_3(g)$ injection and conduct solid phase characterization (during treatment pH12 & post treatment pH 8) to identify dominant mineral phases controlling U behavior.
- **1.2** Study re-oxidation kinetics of Tc-99 in perched and GW that has been initially reduced by strong reductants such as ZVI, SMI and CPS in batch-scale experiments under anaerobic initial conditions followed by aerobic conditions
- **1.3** Conduct characterization of sieved sediment fractions and initiate competitive adsorption experiments on with key contaminants of concern at the max concentrations found at Hanford 200 Area GW and porewater when all contaminants are commingled together to compare adsorption results when each contaminant is present separately.
- **1.4** Determine if glass dissolution behavior is controlled by pH-mediated effect by sediment or by grout-contacted GW at 25°C, 40°C, and 70°C.

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

FIU Applied Research Center

FIU Year 10 Accomplishments:

Ammonia Gas for Uranium Remediation

- Completed Clemson-FIU collaboration on high loading experiments containing higher U loading in phyllosilicate minerals for TEM-EDS analysis
- SEM-EDS statistical analysis shows that there is a significant difference in control vs. aerated-(pH 8) for all phyllosilicate mineral samples
- *Ongoing* – manuscript in preparation for solid phase characterization for ammonia- and aerated-treated phyllosilicate mineral samples

Tc-99 re-oxidation after sequestration with strong reductants

- Obtained and characterized Tc reoxidation in the presence of 0.1% Hepure ZVI, SMI and 0.5% CPS; CPS samples featured the highest Tc reoxidation.
- *Ongoing* - Data analyses of LSC results for CPS amended perched and GW samples.

Competitive adsorption experiments

- Conducted solid characterization studies for Hanford Formation sediment.
- Evaluated literature and Hanford monitoring reports for max and average conc of contaminants.
- *Ongoing* - Initiated competitive sorption experiments

Experimental Support of Lysimeter Testing

- SPFT experiments utilizing grout-contacted groundwater as the leachate
- Characterization of solid samples from the grout-contacted solution
- *Ongoing* - Complete grout experiments at 70°C and analyses of collected samples.

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

- **Publication in *Applied Clay Science,* "Phyllosilicate mineral dissolution…via base treatment".**
- **Manuscript on iodine incorporation in CaCO3 is under review in the AG journal.**
- **Presented results at WM2020.**
- **Manuscript in preparation "Solid phase characterization and transformation of illite mineral under alkaline conditions**

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

Proposed Scope for FIU Year 01*

Site Needs:

DOE-EM faces a number of environmental challenges that are technically complex and unique to EM with tremendous associated cleanup costs. This project is focusing on basic science to fill knowledge gaps and validate potential remediation technologies to assist with environmental cleanup of Hanford Site's contaminated vadose zone and groundwater. This investigation will assist Hanford Site and other DOE EM sites in identification of promising Tc-99 remediation technologies using strong reductants and evaluate attenuation processes that affect the fate and transport mechanisms of comingled contaminants including U (VI), I-129, Tc-99, Cr(VI) and NO_3^-.

Objectives:

- **1.2** Conduct Re-oxidation of Redox Sensitive Contaminants Immobilized by Strong Reductants such as zero valent iron (ZVI), sulfur modified ZVI and calcium polysulfide (to be completed in Year 1)
  - Supports evaluation of potential in situ treatment technologies for the vadose zone, groundwater and perched water zone located within the 200 Area at Hanford
- **1.3** Evaluation of Competing Attenuation Processes for Mobile Contaminants in Hanford Sediments
  - Provide scientific support in evaluation of attenuation processes that affect fate and transport mechanisms of contaminants of concern present in Hanford Site VZ sediment.
- **1.4** Experimental Support of Lysimeter Testing
  - Conduct waste form dissolution experiments both glass and grout in a wide range of pH, temperature and solution composition conditions.

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

FIU Applied Research Center

Site Needs:

Complex and diverse physical and biogeochemical processes are mainly responsible for retaining contaminants in the wetlands at SRS. However, changes in the geochemical conditions could cause the remobilization of 129I. This study will supplement ongoing activities at SRS pertaining to the Area Completion Project and associated permitting strategies to evaluate and meet standards for contaminants in the Four Mile Branch Wetland. NOM has proven to be a viable in-situ treatment technology for uranium remediation in acid conditions. Low cost modified humic substances are potential amendments for treatment of uranium in groundwater associated with F-Area Seepage Basins plume.

Objectives:

- Understand the dominant mechanisms of attenuation of I-129 in wetland sediment and identify environmental conditions that may influence remobilization of previously immobilized I-129.
- Determine if the modified humic acid (KW15 modified Humics) can be used to control the mobility of uranium in groundwater and study the sorption/desorption of U onto SRS sediment coated with modified HA.

Present (FIU Year 10) Subtasks:

- **2.1** Investigate environmental factors controlling the attenuation and release of I-129 from SRS wetland sediments
- **2.2** Batch experiments to study uranium sorption by humate treatment zone created by a modified humic acid. Evaluate the effect of contact time, pH and initial uranium concentrations.

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

FIU Applied Research Center

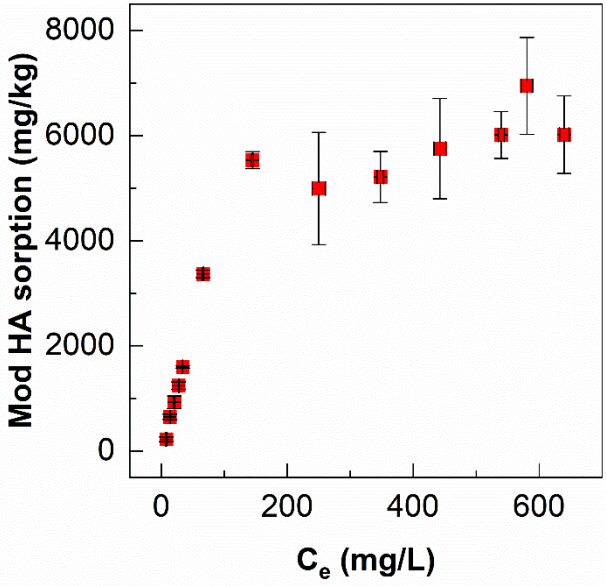
FIU Year 10 Accomplishments:

Environmental Factors Controlling the Attenuation and Release of I-129 from SRS Wetland Sediments

- Characterized SRS wetland sediment using various techniques: sediment size fraction, BET, XRD, sediment pH.
- *Ongoing*:
  - Sediment characterization via SEM/XRF, kinetics of Iodine sorption.

Batch Experiments with Modified Huma-K

- Completed batch desorption experiments with modified humic acid to study the effect of pH (3-8),
- Initiated uranium sorption experiments;
- Compared Huma-K & mod-HA data.
- *Ongoing*: Uranium sorption/desorption experiments.



- Research presented at WM2020 Symposia.
- Manuscript under peer-review in Journal of Environmental Sciences, "Evaluation of a humate amendment to enhance the sequestration of uranium in contaminated groundwater"

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

FIU Applied Research Center

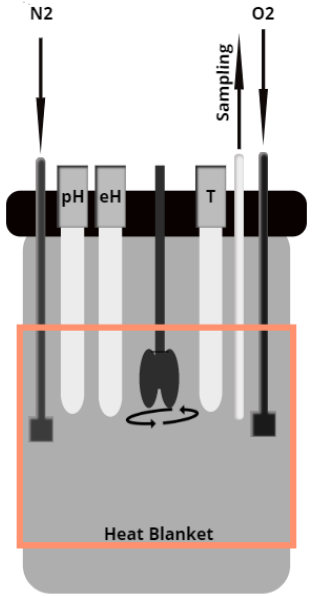
Proposed Scope for FIU Year 01*

Site Needs:

This task will assist SRS with closure of F-Area Hazardous Waste Management Facilities Groundwater Units. The Savannah River Site (SRS) has been proactively researching new innovative strategies for groundwater remediation. Significant data gaps still exist regarding the behavior and chemistry of radionuclides of concern such as I-129 and uranium at SRS and other DOE EM sites.

Objectives:

- **2.1** Investigate geochemical factors controlling the sorption and release of iodine from wetland sediments.
  - Perform batch and microcosm experiments to evaluate the effect of temperature and redox conditions on attenuation and release of I-129 from the seepline/wetland sediments
- **2.2** Finalize uranium sorption studies and initiate experiments with new humic acid material formulated specifically for remediation of heavy metals



Microcosm set up

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

FIU Applied Research Center

Site Needs:

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

Objectives:

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

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

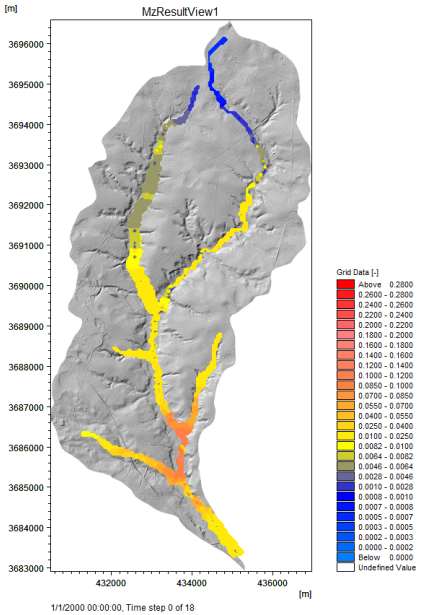
Task 3: Contaminant Fate And Transport Modeling in Tims Branch

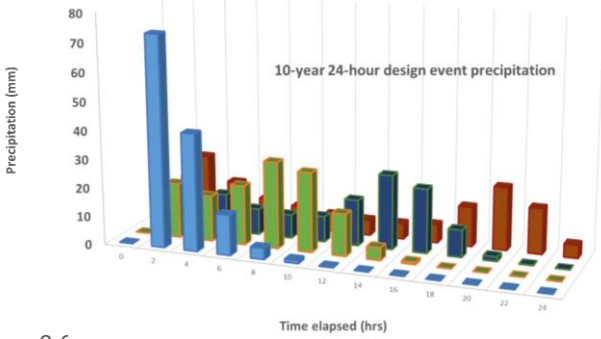
FIU Year 10 Research Highlights

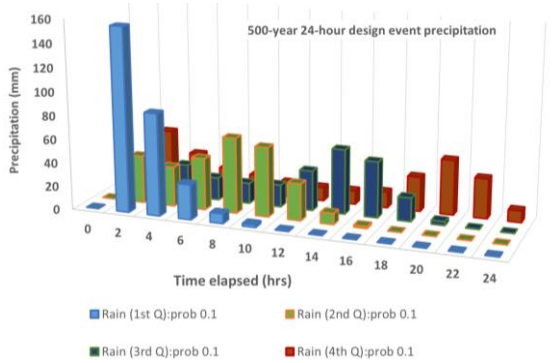
Calibration, Validation and Extreme Events Hydrology Modelling

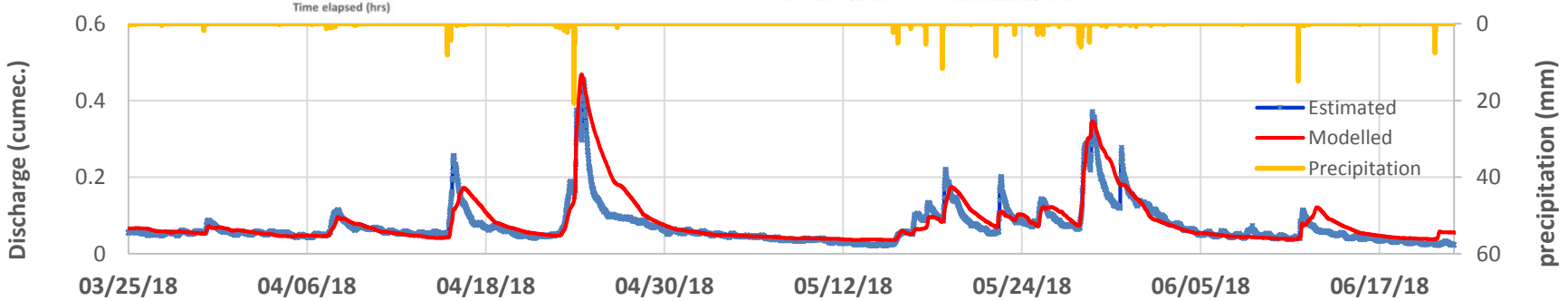
- MIKE SHE hydrology model calibration completed
  - Calibration process reviewed
  - Model parameters assigned based on lit. review and hydrology modeling standards
  - Performed simulations of various extreme event scenarios:
    - ARIs considered: 5yr, 10yr, 25yr, 100yr and 500yr
    - Durations considered: 6hr, 12hr, 24hr and 96hr

Animation: Temporal distribution of Velocity*Flow Depth (U*D) for a 100-year 24-hour design storm event.









Task 3: Contaminant Fate And Transport Modeling in Tims Branch

Research Highlights

Extreme Events Sediment Transport Modelling

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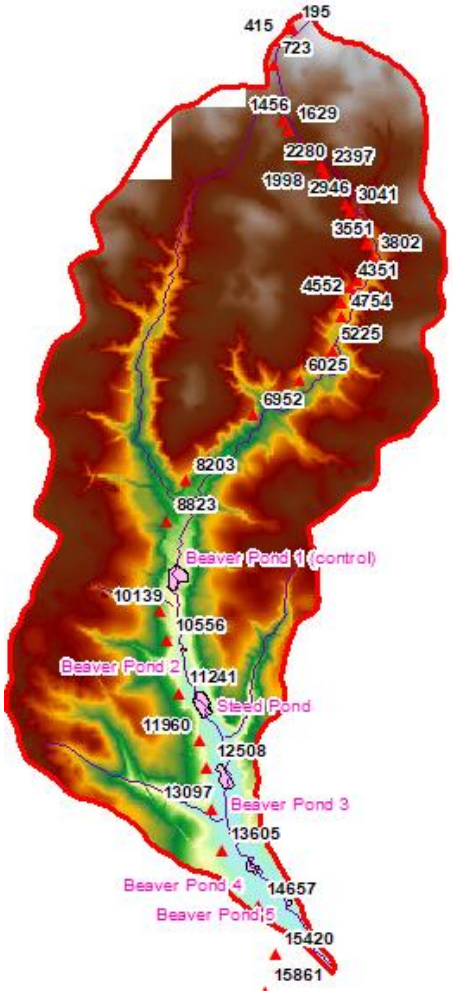


Fall velocity
C - offset: 10.00 g: 4.50 m: 0.00
w0: 0.047000 swi: 0.000392

Deposition
Critical Shear stress 0.200
Time centering 0.80

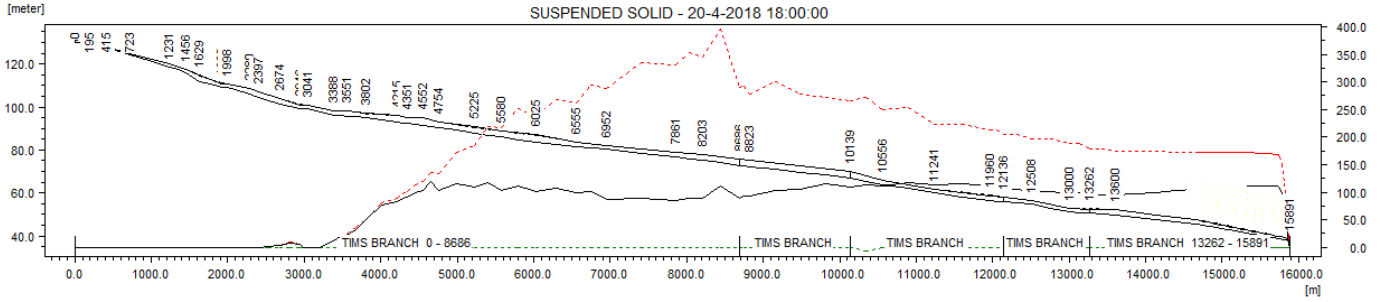
EROSION
Instant erosion of layer 1

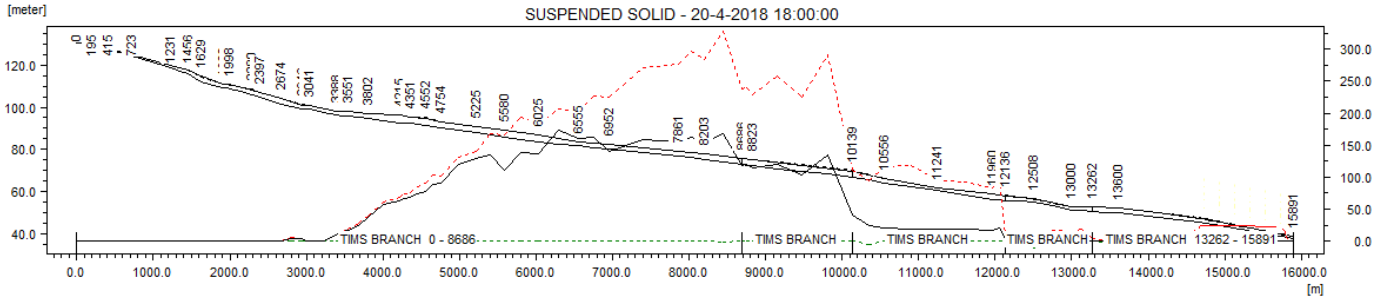
	Sediment layer 1	Sediment layer 2	Sediment layer 3
Critical shear stress	0.211	0.300	0.300
Erosion coeficient	0.20	0.200	0.200
Erosion exponent	3.00	3.000	3.000

Consolidation
Transition rates
Layer1 -> Layer2 2.850
Layer2 -> Layer3 0.150
Sl. fric. coef. 5.00

Scenario 1
D50=6.25e-5
Cr. shear stress, ero.=0.165 N/m^2
Cr. Shear stress, depo.=0.10 N/m^2

Scenario 2:
D50=3.53e-4
Cr. shear stress, ero.=0.2115 N/m^2
Cr. Shear stress, depo.=0.10 N/m^2



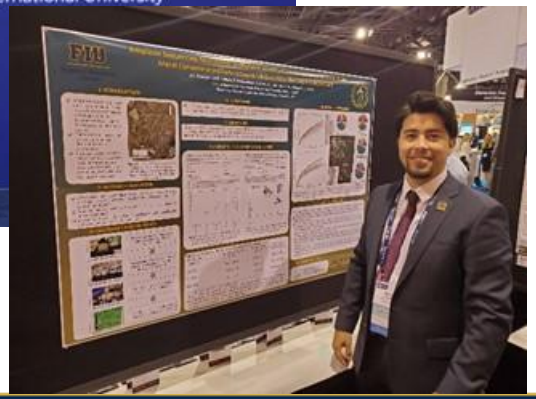


Task 3: Contaminant Fate And Transport Modeling in Tims Branch

Accomplishments

FIU Applied Research Center

- WM20 paper & oral presentation by Dr. Yan Zhou:
  - Zhou, Y., M. Mahmoudi, A. Lawrence, R. Hariprashad, A. Yancoskie, J. Morales, M. Valencia, B. B. Looney, J. C. Seaman. *"Contaminant Transport Modeling for Technology Evaluation and Long-Term Monitoring in the Tims Branch Testbed, SC"*, Proceedings of the Waste Management Symposia 2020, Phoenix, AZ, March 2020.
- DOE Fellow Amanda Yancoskie awarded Roy G. Post Foundation Graduate Scholarship at the WM20 Symposia.
- Amanda also presented poster at WM20 based on her Summer 2019 internship *"2D Dam-Break Analysis of Lake and Par Pond Dams Using HEC-RAS".*
- DOE Fellow Juan Morales presented poster at WM20 based on his Summer 2019 internship *"Amplicon Sequencing Assessment to Measure Microbial Community Response from Heavy Metal Contaminated Soils in Savannah River Site, Tims Branch Watershed"*.
- Juan also completed a10-wk **remote** Summer 2020 internship with PNNL mentored by Dr. Katrina Waters.



Task 3: Contaminant Fate And Transport Modeling in Tims Branch

FIU Year 01* (Sept 2020 - Sept 2021) Objectives

* Assuming new contract number is issued

FIU Applied Research Center

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

- Model optimization to improve and verify Tims Branch model performance
  - Sensitivity analysis, calibration and validation
- Scenario analysis under extreme hydrological conditions to determine stormflow impacts and downstream transport of priority contaminants of concern.
- Download water level data from remote devices in Tims Branch for calibration and validation.
- Travel to SRS to perform routine maintenance and calibration of remote monitoring devices.
- Explore the potential for migration of the data inputs from the Tims Branch model to an open source environment for easier integration with other DOE-EM modeling efforts.

Subtask 3.2: Model Development for the Fourmile Branch (FMB) and/or Lower Three Runs (LTR) Watersheds (NEW)

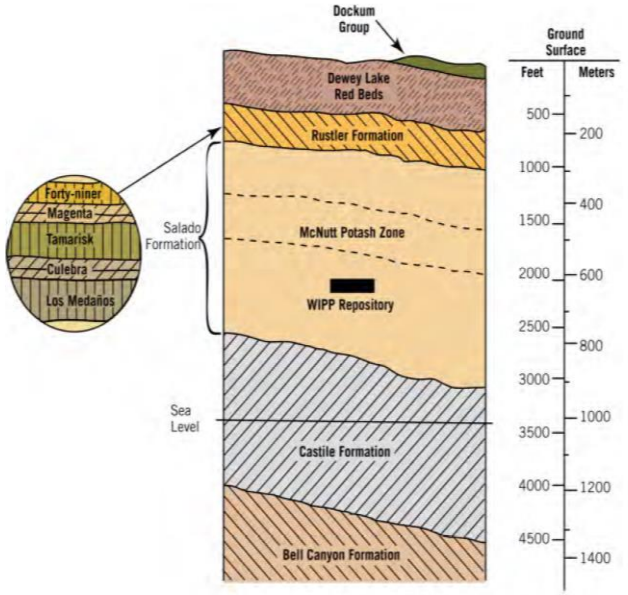
- **Aim:** To develop surface water and sediment transport models of the FMB and/or LTR stream systems to evaluate potential fate and transport of ^{137}Cs in these contaminated watersheds during extreme meteorological events.
- Initiate data collection and pre-processing activities and develop conceptual models.

Task 5 - Research and Technical Support for WIPP

FIU Applied Research Center

Site Needs:

This research efforts aimed to assist the LANL ACRSP team to better understand the long-term fate and transport of the actinides in the Waste Isolation Pilot Plant (WIPP). Specifically, the effects of ligands in the waste stream (e.g. EDTA) on near field mobility of actinides is still unknown (*Dunagan, 2007; Brush, 1990*). Complexation constants have been measured for most actinides and lanthanides (*Thakur et al., 2014; 2015; Borkowski et al., 2001*). However, their long-term stability and sorption are not fully understood in high ionic strength systems. EDTA presents a major risk factor due to its significant occurrence in repository waste (0.3 mM) (*Roach et al., 2008*).



FIU Year 10 Objectives:

- To understand the interactions between actinides and WIPP-relevant ligands and minerals and their potential fate in the subsurface.
- Measure dissolution of dolomite in variable ionic strength matrices with and without EDTA

Present Tasks:

- Update sorption data for the actinides that will indirectly support performance assessment models for WIPP
- Measure sorption parameters for Nd(III), Th(IV), and U(VI) onto iron oxide in WIPP-relevant brines, GWB and ERDA-6 under anoxic conditions

Oxidation State Distribution of Key Actinides in WIPP Performance Assessment

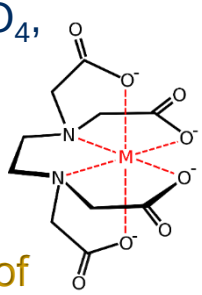
Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Plutonium	50%	50%			Am/Nd for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium

Task 5 - Research and Technical Support for WIPP

FIU Applied Research Center

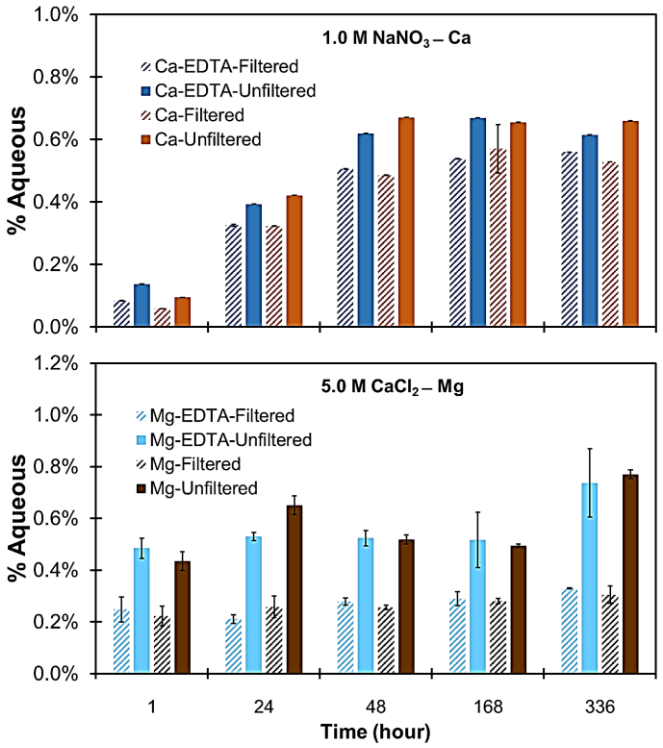
FIU Year 10 Research Highlights:

- Completed batch experiments evaluating the impact of EDTA, ionic strength and ions on dissolution of dolomite in 0.1- 5.0 M NaCl, $MgCl_2$, $CaCl_2$, $NaNO_3$, Na_2SO_4, CsCl, and $Na_2B_4O_7$



FIU Year 10 Accomplishments:

- A poster titled "the impact of EDTA on sorption of Nd(III), Th(VI) and U (VI) onto dolomite in WIPP-relevant brines, GWB and ERDA-6 was presented at WM2020 conference in Phoenix, Arizona (March 2020)
- DOE Fellow Alexis Vento presented a poster on "dolomite dissolution in variable ionic strength systems relevant to the WIPP at Waste management symposia, Phoenix Arizona (March 2020)



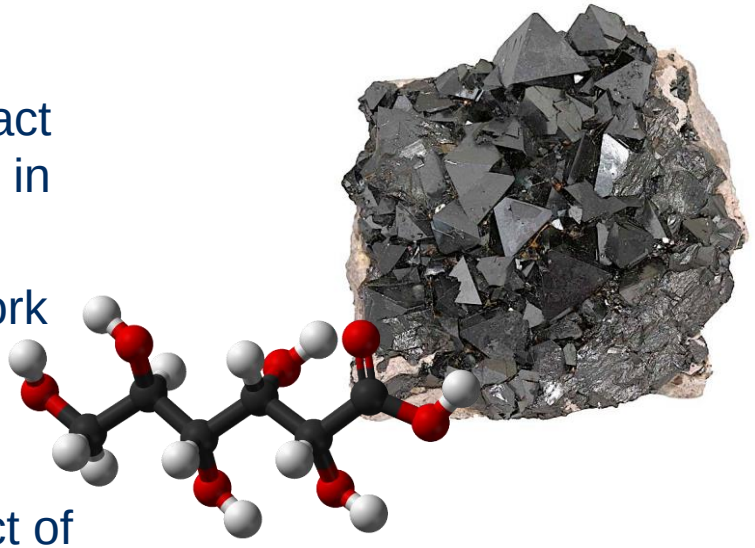
Aqueous fractions of Ca^{2+} (orange/dark blue) in 1.0 M $NaNO_3$ (top) and Mg^{2+} (brown/light blue) in 5.0 M $CaCl_2$ (bottom) with and without EDTA. Stripped are filtered and solids are unfiltered samples

Task 5 - Research and Technical Support for WIPP

FIU Applied Research Center

Upcoming for FIU Year 10:

- Complete collections/analyses of data on the impact of EDTA/ionic strengths on dissolution of dolomite in WIPP-relevant matrices
- Visit LANL collaborators to discuss updates for work supporting the WIPP



Objectives for FIU Year 01*:

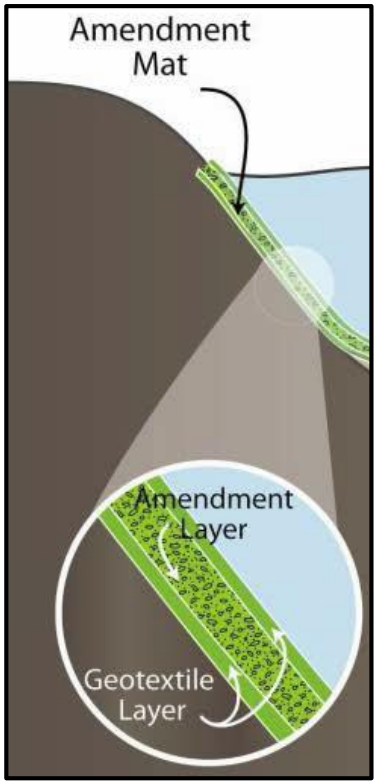
- Conduct batch experiment investigating the impact of gluconate on the sorption of contaminants onto various iron oxide minerals in high ionic strength systems under anoxic conditions
- Continue experimental support through identification of minerals and ligands of interest to the WIPP (iron oxides, key contaminants with co-located lead) for risk assessment models for the WIPP re-certification.

Task 7 – Research and Technical Support for Oak Ridge Reservation (NEW)

FIU Applied Research Center

FIU Year 01* Objectives: Multi-Layer Reactive Mat for Hg Remediation

- Conduct experiments evaluating the effectiveness of a suite of multi-layer sorbents for Hg sequestration
- Conceptualize/engineer Hg-sequestrating sorbents stacked between layers of porous geotextile mat
- Evaluate the geotechnical properties and long-term effectiveness of the multi-layer reactive mat
- Optimize engineering parameters, and deploy a prototype of the multi-layer reactive mat at a test site in East Fork Poplar Creek on the Oak Ridge Reservation (ORR)



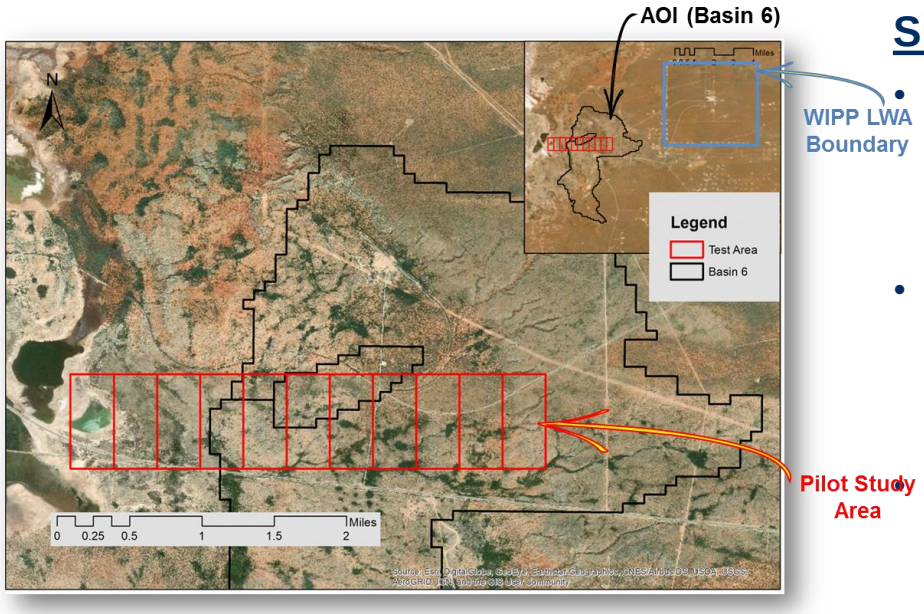
Future Objectives:

- Continue work on advanced sorbent development in support of mercury remediation efforts in East Fork Poplar Creek.
- Conduct applied research addressing technical challenges related to design/engineering parameters and long-term effectiveness of proposed Hg-sequestering sorbents for mercury cleanup at ORR.

Task 6: Hydrology Modeling for WIPP

Area of Interest (AOI)
Basin 6

Pilot Study Area
Small representative area within Basin 6, west of the WIPP Land Withdrawal Act (LWA) Boundary



Site Needs:

- Improved understanding of regional water balance, particularly relationship between Culebra recharge and intense, episodic precipitation events typical of the monsoon.
- Understanding of rate of propagation of shallow dissolution front, and impact of land use changes around the WIPP facility on water levels in compliance-monitoring wells.
- Revision of current site conceptual model needed to couple SW and GW processes, which both require a high-res DEM including channels and sink holes to account for surface water routing and return flow.

Objectives:

- Development of a GWM for the WIPP site using the DOE-developed Advanced Simulation Capability for Environmental Management (ASCEM) modeling toolset to improve the current understanding of regional and local groundwater flow at the WIPP site.
- An open source LSM will also be used to provide surface process parameters for input into the ASCEM model (e.g. infiltration rate) to compute the surface water balance, across multiple scales and reduce uncertainties in recharge estimates and propagation of the shallow dissolution front.

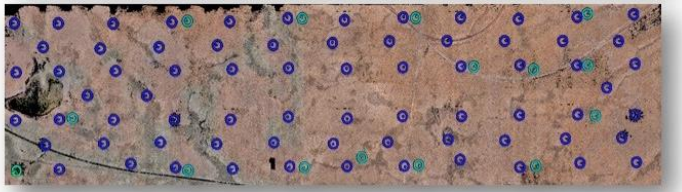
Task 6: Hydrology Modeling for WIPP

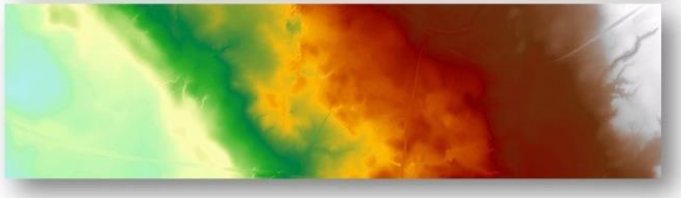
Research Highlights

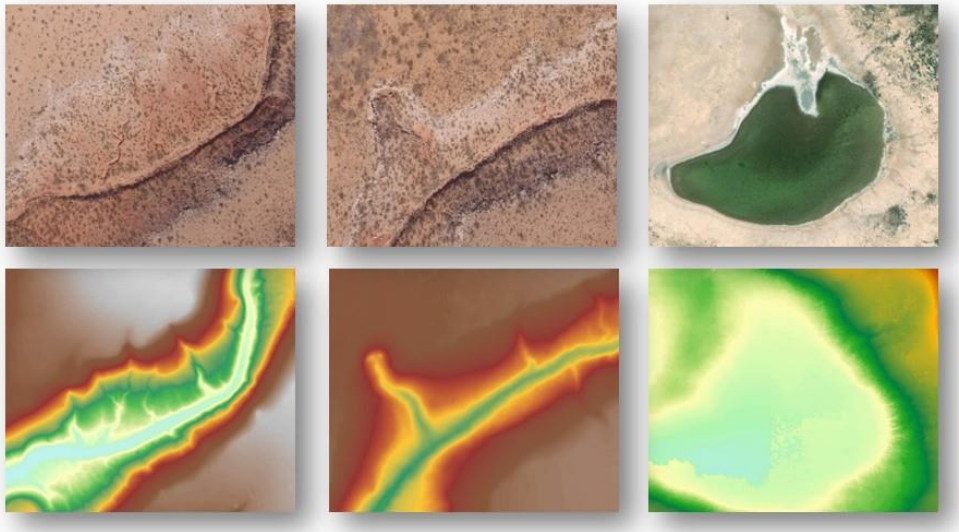
Subtask 6.1: DEM and Hydrologic Network

Procedure:

- Ground control point (GCPs) surveying
- Automated aerial image collection
- Image processing using Pix4D
- Geo-referencing using GCPs







Gully | Land Sink | Brine Lake

Results:

- 5 km^2 DEM, up to 0.05 m resolution
- Significant topographical/hydrological features are easily identifiable.

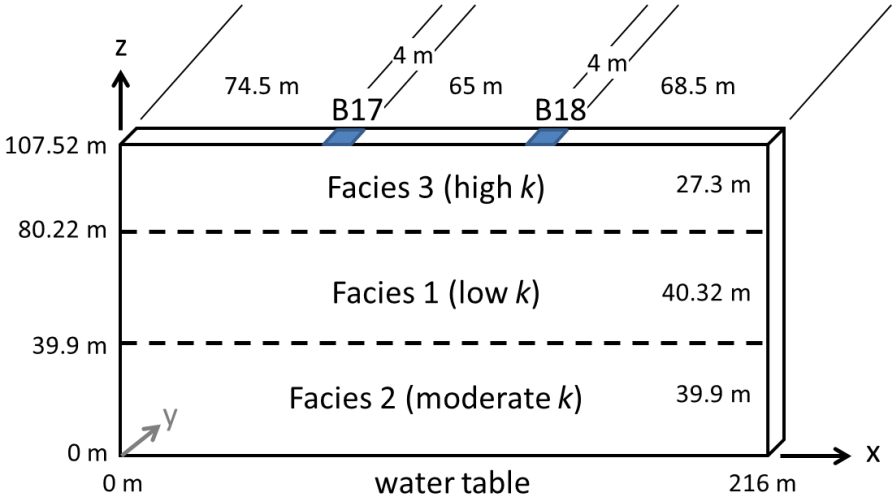
Additional Research:

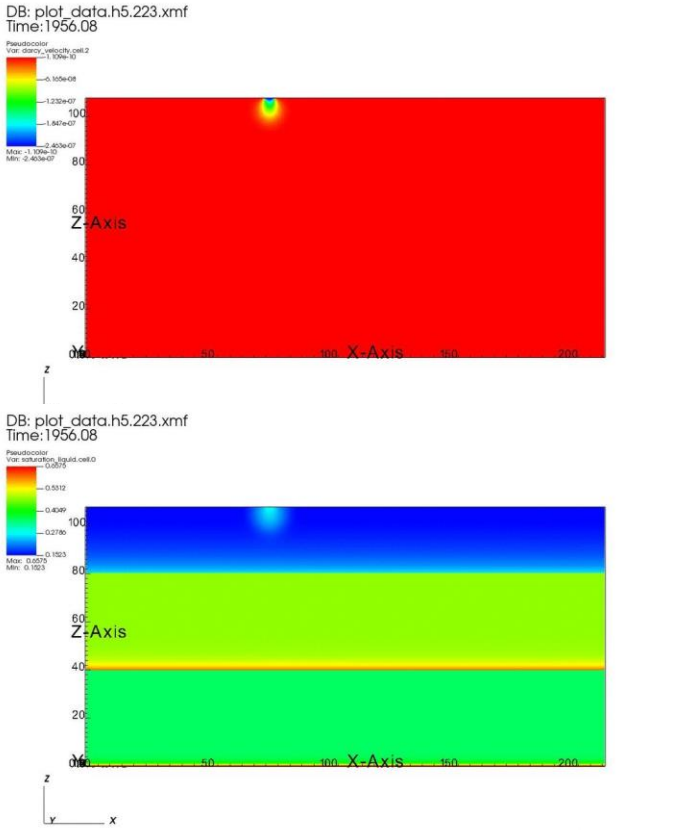
- Eval. of vegetation removal methods

Task 6: Hydrology Modeling for WIPP
Research Highlights
Subtask 6.2: Model Development

Land Surface Model
- WRF-Hydro (Weather Research and Forecasting)

ASCEM Groundwater Model (GWM)
- Water/solute movement
- On-going training





Task 6: Hydrology Modeling for WIPP
Accomplishments

DOE Fellow Gisselle Gutierrez:

- Presented poster at WM20 Symposia *"Evaluation of Techniques for Vegetation Removal from UAV-based Photogrammetric DSM Near WIPP Land Withdrawal Act Boundary, NM" based on this project work.*
- Awarded Roy G. Post Foundation Undergraduate Scholarship at WM20 Symposia.
- Graduated with BS in Env. Eng. Summer 2020. Pursuing MS in Civil Eng. with focus in Water Resources and continuing as DOE Fellow assigned to WIPP Hydrology Modeling task.
- Completed 10-wk **remote** Summer 2020 internship with CBFO mentored by Dr. Anderson Ward.

Task 6: Hydrology Modeling for WIPP

FIU Year 01* (Sept 2020 - Sept 2021) Objectives

* Assuming new contract number is issued

FIU Applied Research Center

Subtask 6.1: Digital Elevation Model (DEM) and Hydrologic Network

- Capture high-res imagery of entire Basin 6 west of the WIPP in Nash Draw area using UAV.
- Process imagery using state-of-the-art photogrammetric techniques to build high-res DEM.
- Delineate stream channel and other relevant hydrologic features to support model development.

Subtask 6.2: Model Development

- Initiate development of LSM of Basin 6 that provide parameters that account for variations in surface processes, i.e., land use and climatic changes.
- Initiate development of ASCEM GWM using parameters acquired from LSM (i.e., spatial distributed recharge) to simulate water table fluctuation and estimate the rate of halite dissolution and propagation of the shallow dissolution front, which both have potential to affect post-closure repository performance.
- Train FIU's research personnel/students on selected LSM & ASCEM to execute scope.
- Train undergraduate/graduate students (DOE Fellows) on UAV photogrammetry methods and provide mentorship and field experience through student summer internships in collaboration with CBFO and PNNL scientists.