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Project Staff and Students



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Project Clients and Collaborators



- DOE EM-12
 - Patricia Lee FIU Project Liaison
 - Latrincy Bates SRNL Project Liaison
- DOE EM-13
 - Albes Gaona Project Liaison & Sustainable Remediation Task Lead
 - Andrew Szilagyi Director of D&D Operations
- SRNL
 - Carol Eddy-Dilek Project Liaison
 - Miles Denham Task 1 Lead
 - Brian Looney Task 2 Lead
 - Ralph Nichols Task 3 Lead



Project Description



Background/History

- Integrated surface/subsurface flow & contaminant transport models of ORR watersheds (East Fork Poplar Creek, Upper EFPC (Y-12 NSC Area) and White Oak Creek).
- Expt'l studies to obtain kinetic/equilibrium data parameters related to Hg transport, speciation and methylation/demethylation kinetics within EFPC watershed.
- GIS technology for storage and geoprocessing of spatial/temporal model data.

New scope (FY13 – Year 4):

- Level 2 (semi-quantitative) Green & Sustainable Remediation (GSR) analysis at DOE sites.
- Analysis of the baseline, optimization studies and development of system improvement plan for A/M Area groundwater remediation system at SRS.

Transition from ORR to SRS (FY14 – Year 5):

• Experimental studies, modeling efforts and sustainability studies now focused at SRS.



Project Description



FIU Year 4 Carryover Work Scope

- Task 1: EFPC Model Update, Calibration and Uncertainty Analysis Tech. Rpt
- Task 2: Simulation of NPDES- and TMDL-Regulated Discharges from Non-Point Sources for the EFPC and Y-12 NSC – Technical Report
- Task 3: Sustainable Remediation and Optimization: Cost Savings, Footprint Reductions, and Sustainability Benchmarked at EM Sites – Technical Report
- Task 4: Geodatabase Development for Hydrological Modeling Support Technical Report

FIU Year 5 New Work Scope

- Task 1: Modeling of the Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems
- Task 2: Surface Water Modeling of Tims Branch
- Task 3: Sustainability Plan for A/M Area Groundwater Remediation System



DOE-FIU Cooperative Agreement

Project 3 Accomplishments

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Project-Wide Major Accomplishments



Completion of FIU Year 4 Carryover Work Scope

- Task 1 Final Technical Report: "EFPC Model Update, Calibration, and Uncertainty Analysis"
 - Submitted July 31, 2014.
- Task 2 Final Technical Report: "Simulation of NPDES- and TMDL-Regulated Discharges from Non-Point Sources for the EFPC and Y-12 NSC"
 - Submitted July 31, 2014.
- Task 3 Final Technical Report: "Green and Sustainable Remediation Practices, Tools and their Application at DOE Office of Environmental Management Sites"
 - Submitted September 26, 2014.
- Task 4 Final Technical Report: "Geodatabase Development for Hydrological Modeling Support"
 - Submitted June 30, 2014.





Task 1: EFPC Model Update, Calibration, and Uncertainty Analysis (Yr 4 Carryover)

- Subtask 1.1: Review of the existing Hg thermodynamic database and update for EFPC environmental conditions.
- Subtask 1.2: Integration of the Hg thermodynamic database into the existing EFPC model.
- Subtask 1.3: Provide a series of simulations using the EFPC model and the thermodynamic and kinetic interactions.



Carryover Work Scope: Task 1



Objective

Analysis of coupling between hydrology and Hg transport within context of decreasing risk of D&D activities.

Benefits

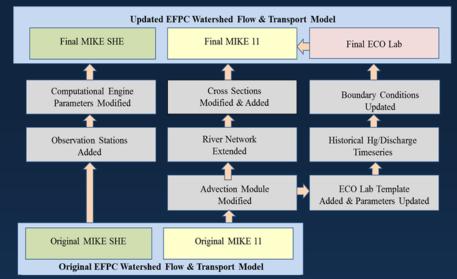
- Conventional hydrologic and remediation analytical tools (accepted by EPA, USACE, and USGS) in combination with latest scientific software (2D/3D numerical flow and transport models integrated with reaction kinetics and thermodynamic software) provides integrated solution for understanding mobility and impacts of contaminants at DOE sites.
- Provides state-of-the-practice tools for analysis of sustainable and green remediation alternatives (developed for DOD sites) needed to address long term sustainability in terms of reduced environmental and energy footprints of remedial actions.



Carryover Work Scope Task 1 Accomplishments



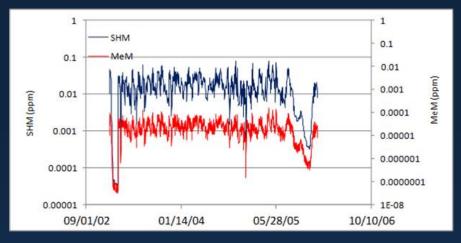
- Developed & calibrated numerical model for hydrology, sediment & Hg transport in UEFPC (1996 to present).
- Reconfigured model to incorporate sedimentation module and extended it to include 52 additional outfalls covering entire EFPC and Bear Creek.
- Performed simulations using range of Manning's numbers, threshold run-off water depths, and drainage coefficients to calibrate flow from 2000 – 2008. MATLAB scripts were used for statistical analysis of observed and computed data.
- Provided DOE with assessment reports on effectiveness of 8 remedial scenarios.





Carryover Work Scope Task 1 Accomplishments

- Reviewed and updated existing Hg thermodynamic database specific to EFPC environmental conditions & integrated it into flow and transport models already developed for the site.
- Implemented equations in the kinetic solver (ECOLAB) which provides distribution between total-Hg and methyl-Hg species based on observed distribution coefficients (as fraction).
- Conducted preliminary tests to calibrate model using observed ratios of total-Hg and methyl-Hg concs. Initial results showed template predicts ratio between total-Hg and Me-Hg concs.



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Figure showing nearly proportional distribution between dissolved mercury (SHM) and methylmercury species (MeM) based on the ECOLAB kinetic model.





Task 2: Simulation of NPDES- and TMDL-Regulated Discharges from Non-Point Sources for the EFPC and Y-12 NSC (Yr 4 Carryover)

 Subtask 2.1: Use of the observed outfall discharges to provide simulations of the entire EFPC watershed and the load discharge at Station 17 using the EFPC model previously developed with MIKE SHE and 11.



Carryover Work Scope: Task 2



Objective

Use of EFPC model for numerical analysis of contaminant flow and transport within EFPC watershed to determine impact of model parameters on TMDL.

- Ecosystem responses to variations in contaminant loading (changes in external & internal loading in time and space).
- Effect of ecosystem restoration on existing contaminant pools.

Benefits

- Modeling supports development of TMDLs to estimate source loading and evaluate loading capacities that meet WQ standards.
 - EFPC identified on Final 2008 303(d) List by TDEC as impaired waterbody not supporting designated uses due to contamination by mercury, PCBs, nitrates, and phosphates.
- TMDL may be used to develop controls for reducing pollution from point and nonpoint sources to restore and maintain WQ.



Carryover Work Scope Task 2 Accomplishments

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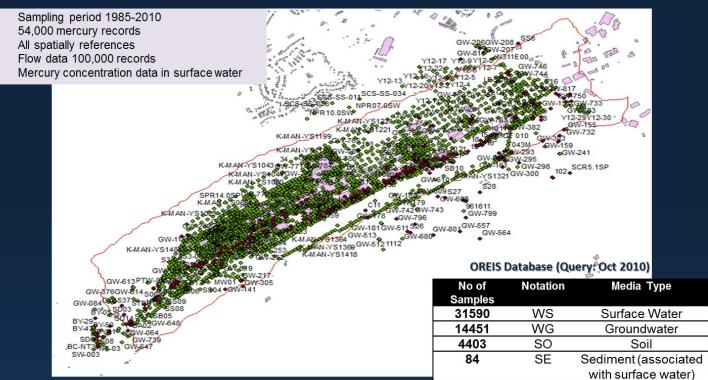
- Surface and GW levels
- Water flow
- Spatiotemporal distribution of pollutants in soil, water, and sediments
- Bioassessment data
- Spatial and temporal analyses conducted to:
 - Identify spatial variations of Hg in EFPC water, shallow/deep soil layers, stream bank/streambed sediments
 - Evaluate timing of impairment, potential source loading, other conditions contributing to impairment
 - Investigate effect of rainfall and runoff on Hg conc. in EFPC

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Carryover Work Scope Task 2 Accomplishments

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Mercury Concentrations in Soil in the Watershed Model Domain

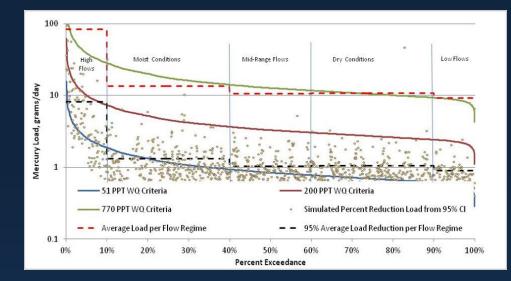
 Data (up to 2013) for all 57 outfalls along EFPC obtained from OREIS and formatted for input into model and boundary conditions (rainfall, evapotranspiration, timeseries of outfalls, rivers and canals) updated to extend simulations to 2012.



Carryover Work Scope Task 2 Accomplishments



- Target Hg conc. for EFPC = 51 ppt for recreational use (TDEC regulations for surface waters), from which "Loading Capacity" duration curve was developed.
- Several target load-duration curves developed for EFPC
 - Hg target concs. of 51, 200, and 770 ppt applied to each ranked flow to generate flow duration curve.
 - Target load reduction criteria developed using % reduction.



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- Model used with newly developed ECOLAB template.
- Incorporates MeHg into kinetic & thermodynamic eqns.



Carryover Work Scope Task 2 Accomplishments

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- Report containing:
 - WQ criteria and TMDL target
 - WQ assessment and deviation from TMDL target
 - WQ data analysis and source identification
 - Development of flow and load duration curves
 - Load allocation analysis





Task 3: Sustainable Remediation and Optimization: Cost Savings, Footprint Reductions, and Sustainability Benchmarked at EM Sites (Yr 4 Carryover)

- Subtask 3.1: Benchmarking of current methodology using SITEWISE[™]
- Subtask 3.2: Implementation of a SITEWISE[™] module for sustainable analysis and optimization of monitoring programs.
- Subtask 3.3: Calibration and Verification of the SITEWISE[™] monitoring program module.



Carryover Work Scope: Task 3



Objectives

Task focused on EM pilot studies and software to:

- Evaluate benefit of sustainable remediation practices.
- Quantify environmental footprint of remedial and other alternatives.
- Develop sustainable optimization module for monitoring program analysis on EM sites.

Benefits

- Building block approach will reduce redundancy in sustainability evaluation and facilitate identification of specific activities with greatest environmental footprint.
- The methodology employed will provide a decision matrix for remedy selection, design, or implementation and allows for a remedy optimization stage as well.



Carryover Work Scope Task 3 Accomplishments



- Software used to downsize a compliance monitoring program (i.e., remove wells, analytes, or frequencies).
- Tests conducted with SITEWISE[™] monitoring module and results used to calculate the following using MS Excel:
 - Reduction in emissions
 - Energy and water usage
 - Waste generation
 - Accident risk over the program total life cycle
- Initial simulations conducted, data gaps identified.



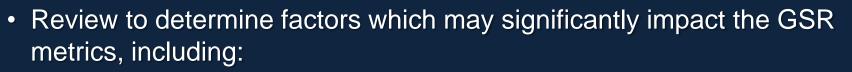
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SITEWISE site info sheet.



Carryover Work Scope Task 3 Accomplishments

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- Excessive number of monitoring locations
- Inefficient chemical injection strategy
- Excess quantity of chemicals used
- Inefficient power usage by over-sized equipment
- Installing less energy efficient equipment
- Unnecessary continuously running equipment
- Unnecessary unit operations
- Development of optimization strategies for integrated surface and GW models capable of predicting contaminant F & T within site domain to achieve the following:
 - Reduction of the number of monitoring locations
 - Improvement of the chemical injection strategy
 - Reduction of the quantity of chemicals used





(Carryover) Task 4: Geodatabase Development for Hydrological Modeling Support

- Subtask 4.1: Update of existing EFPC geodatabase.
- Subtask 4.2: Development of customized Python scripts to enhance database querying capabilities.
- Subtask 4.3: Use the existing geodatabase structure developed for the EFPC modeling work at OR to create similar databases.



Carryover Work Scope: Task 4



Objectives

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

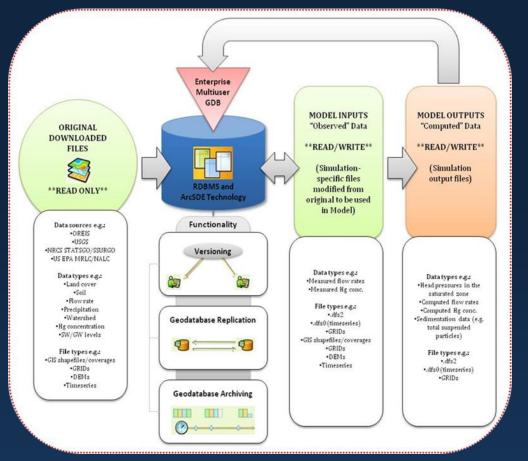
Benefits

- Centralized data management for storage, concurrent editing and import/export of model-specific data.
- Pre-processing and integration of data derived from multiple sources into a single manageable system.
- Automation and simplified retrieval of stored GIS and timeseries data resulting in faster and more complex analyses of field test data. Toolbox created is a scalable and reusable application that can be implemented at other DOE sites.
- Visualization of model-derived research results via maps, graphs and reports.
- Database structure enables linkage with scalable hydrologic modeling applications.
- XML-based GIS data exchange system facilitates import/export of preconfigured data as XML files which can contain both the data definition and the data itself.



Carryover Work Scope Task 4 Accomplishments

Development of enterprise geodatabase to store, process and manage hydrological modeling data derived from FIU's work at ORR.



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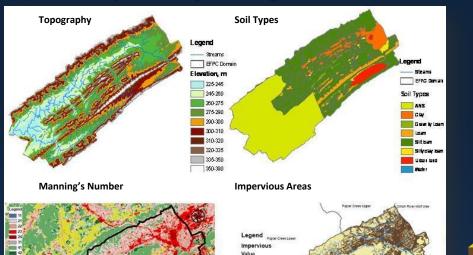
ORR Geodatabase Architecture

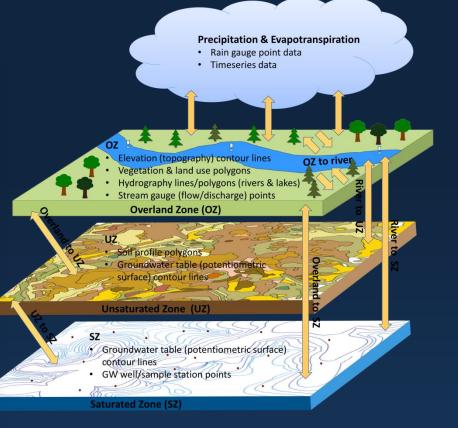


Carryover Work Scope Task 4 Accomplishments

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Pre- and post-processing of spatial and temporal hydrological model data.





GIS-based Model Grid Files

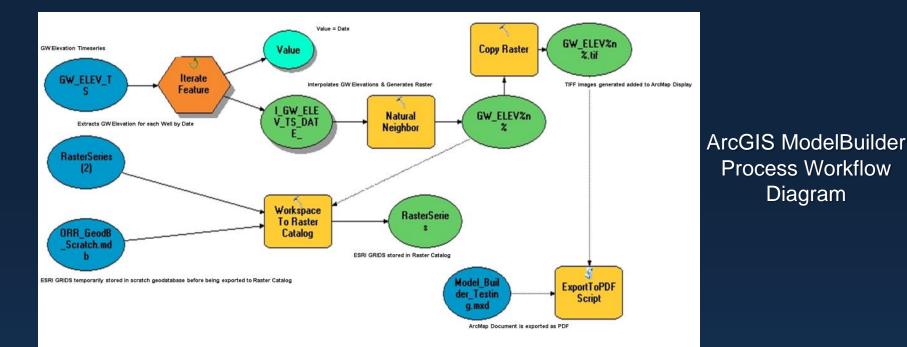
MIKE SHE Model Spatiotemporal (GIS) Data Inputs

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Carryover Work Scope Task 4 Accomplishments

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Development of process flow models & customized Python scripts to automate repetitive querying and geoprocessing of data, generation of maps and reports, and statistical analyses.



Project-Wide Major Accomplishments



FIU Year 5 Work Scope

Milestone No.	Milestone Description	Status
2014-P3-M1	Completion of work plan for experimental column studies (Subtask 1.1)	Completed 9/30/14
2014-P3-M2	Completion of literature review (Subtask 2.2)	Completed 03/31/15
2014-P3-M3	Development of preliminary site conceptual model of Tims Branch (Subtask 2.2)	Completed 03/31/15
2014-P3-M4	Completion of Baseline Analysis (Subtask 3.1)	Completed 2/27/15
2014-P3-M5	SRS site visit and meeting	FIU visited SRS 8/5/14
2014-P3-M6	Meeting and presentation of project progress at SRS	Due 3/18/15, Planned 4/13/15



Project-Wide Major Accomplishments



FIU Year 5 Work Scope

No.	Client Deliverables	Status
1	Draft Project Technical Plan	Submitted 6/18/14
2	Work plan for experimental column studies (Subtask 1.1)	Submitted 9/30/14
3	Literature review summary (Subtask 2.2)	Submitted 3/31/15
4	Baseline analysis summary (Subtask 3.1)	Submitted 2/27/15
5	Two (2) abstract submissions to WM 2015 Symposium	Submitted 8/15/14
6	Presentation overview to DOE HQ/SRNL of the project progress and accomplishments (Mid-Year Review)	3/31/15





New Task 1: Modeling of the migration and distribution of natural organic matter injected into subsurface systems

- Batch & column expts. to determine transport parameters for modeling migration/distribution of humic acid (HA) injected into subsurface.
- Modeling coupled to column studies to address complexities not currently addressed in available models (i.e., spatial and temporal changes in pH and organic properties).
 - Subtask 1.1: Work plan for experimental column studies.
 - Subtask 1.2: Column testing of migration/distribution of HA injected into subsurface systems.
 - Subtask 1.3: Development of subsurface flow, fate and transport model of HA.





Background:

- SRS a major DOE facility for plutonium production during Cold War
- F-Area seepage basins received ~1.8 billion gal. low-level waste
 - Nitric acid, various radionuclides and dissolved metals
- U(VI) and other radionuclides above MCLs
- Humic substances (HS)
 - Account for 50-80% of organic carbon in soil/sediment
 - Excellent binding capacity for metals makes HS strong candidate for remediation efforts to reduce U(VI) mobility in the subsurface



Huma-K





Objectives:

- Assemble, integrate and develop a practical and implementable approach to quantify and model potential natural organic matter
- Understand sorption behavior of HA at varied pH
 - Analyze the mobility of HA injections
 - Predict migration and distribution of humate injected into subsurface systems during deployment for in situ treatment

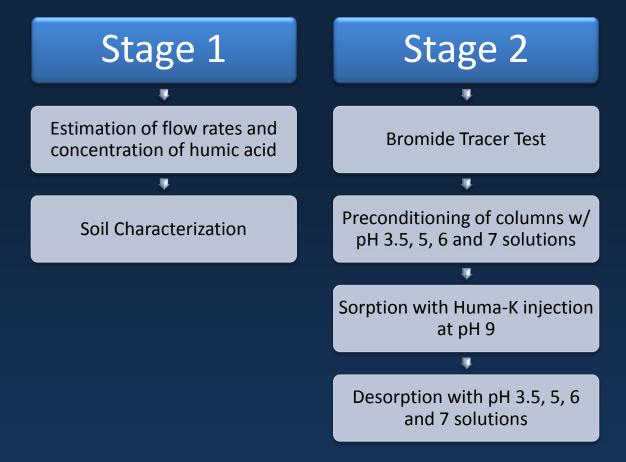
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Project 3 - Task 1 Accomplishments



Completed Subtask 1.1: Work plan for experimental column studies.

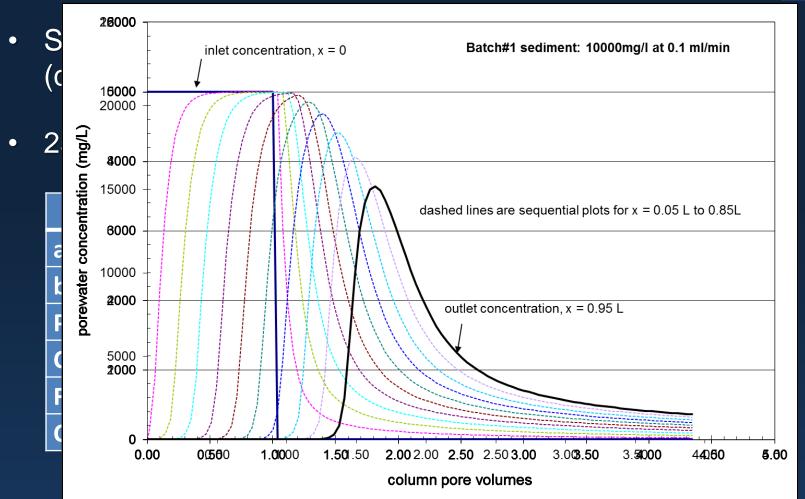


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Project 3 - Task 1 Accomplishments





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Project 3 - Task 1 Accomplishments

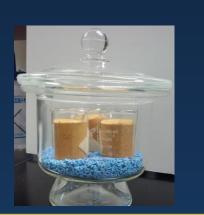


Stage 1: Soil Characterization

- Characterized FAW-1: 60'-70' SRS soil to obtain bulk density, particle density, porosity and pH
 - Bulk density = 1.33 g/cm³
 - Particle density = 2.65 g/cm³
 - Porosity = 0.50
 - pH = 4.06









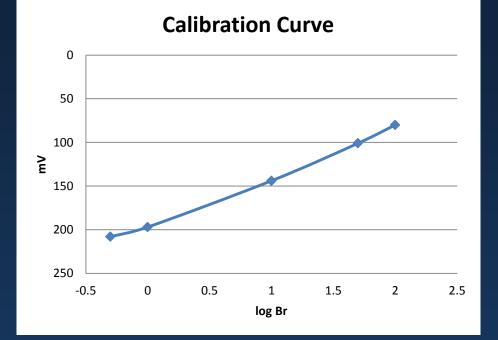
Project 3 - Task 1 Accomplishments



Stage 2: Bromide Tracer Test (Calibration of Bromide Electrode)

- A set of calibration standards in the range of 0.5 to 100 ppm were prepared using DI water and bromide in 20 mL bottles
- Ensures reliability of readings for bromide tracer tests





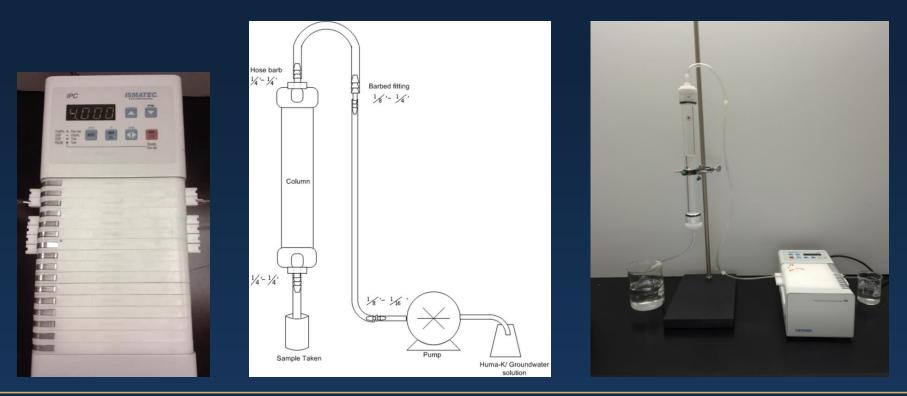


Project 3 - Task 1 Accomplishments



Stage 2: Designed column set-up/configuration to run humate injection experiments

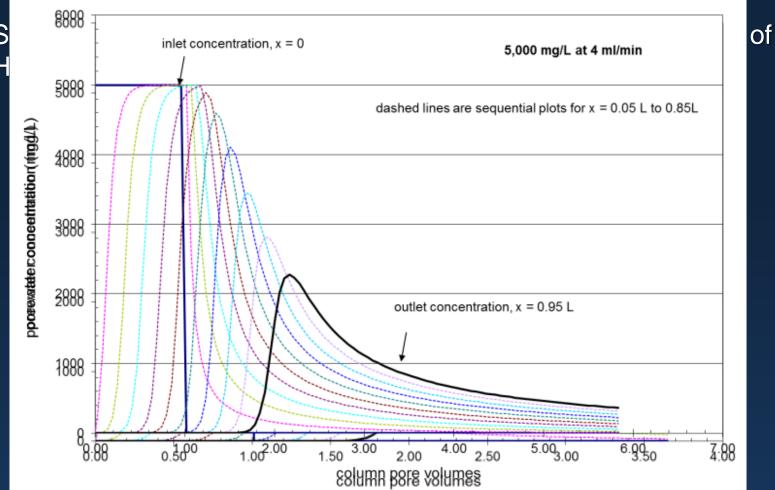
Identified tubing and adapters for pump to achieve required flow rates





Project 3 - Task 1 Accomplishments







Task 1: Future Work – FY14 (Year 5)



- Complete Subtask 1.2: Column testing of migration/distribution of HA injected into subsurface systems.
 - Finish column experiments to determine sorption and desorption properties
 - Determine HA concentration using UV-Vis, iron and silica concentration using ICP-OES
 - Determine transport parameters for modeling migration and distribution of HA injected into subsurface
- Complete Subtask 1.3: Development of subsurface flow, fate and transport model of HA.

CLIENT DELIVERABLES	DUE DATE		
Technical Report for Task 1: Modeling of the migration and distribution of natural organic matter injected into	6/3/15		
subsurface systems			



Task 2: Description



New Task 2: Surface Water Modeling of Tims Branch

- Tims Branch impacted by 60 yrs of anthropogenic events associated with discharges from process and laboratory facilities.
- Application of GIS & stream/ecosystem modeling tools to examine response of Tims Branch to historical discharges and Environmental Management remediation actions.
- Hydrological modeling of Tims Branch (water, sediment, Hg & Sn)
 - Subtask 2.1: Development of a detailed GIS-based representation of the Tims Branch ecosystem.
 - Subtask 2.2: Modeling of surface water and sediment transport in the Tims Branch system.



Project 3 - Task 2 Accomplishments



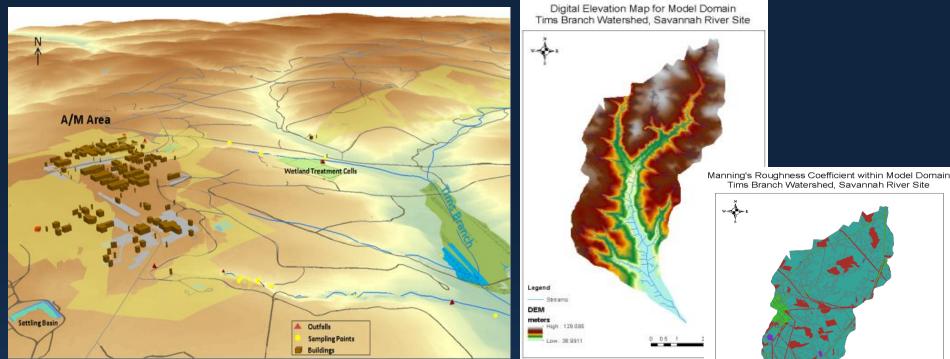
Subtask 2.1: Development of a detailed GIS-based representation of the Tims Branch ecosystem.

- Developed process flow models using ArcGIS ModelBuilder to:
 - Clip GIS data provided by SRNL to model domain.
 - Project data into same coordinate system.
- Developed 2D & 3D GIS-based representations of SRS A/M Area:
 - Tims Branch, major tributaries, water bodies, watershed boundary, SRS boundary, outfalls, sampling/monitoring points, control structures, buildings, roads, topography DEM, elevation contours, soils, etc.
- Developed grid files for MIKE SHE model input from existing GIS data and literature review data:
 - Manning's Roughness coefficient, paved runoff coefficient, infiltration, etc.

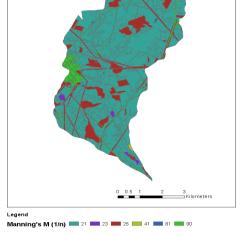


Project 3 - Task 2 Accomplishments





3D Map of SRS A/M Area and Tims Branch (left), Digital elevation model (center) and Manning's roughness coefficient (right) grid files used in MIKE SHE model.





Project 3 - Task 2 Accomplishments



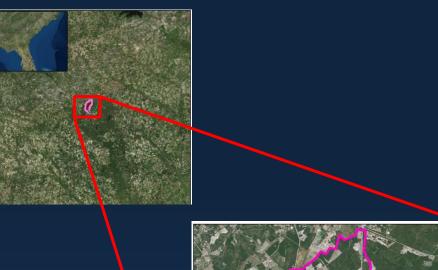
- Subtask 2.2: Modeling of surface water and sediment transport in the Tims Branch system.
 - Completed Literature Review and submitted Summary Report 3/31/15.
 - Reviewed SRS-DOE reports and published journals provided by SRS.
 - More than 30 reports and 100 journal articles reviewed.
 - Total of 10 specific reports found significant were included in the literature review summary report.
 - Specific reports by Brian Looney (2010, 2012) and Betancourt (2011) were among the most addressed in the literature review.
 - Total of 40 journal articles were found relevant to the study.
 - Additional literature review was performed to explicitly address previous hydrological modeling efforts conducted for Tims Branch. Very few studies were conducted in hydrological model development.

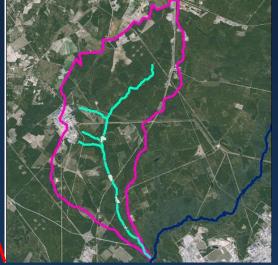


Project 3 - Task 2 Accomplishments



- Developed data-driven conceptual model of Tims Branch.
- Developed a process-based conceptual model.
- Conducted preliminary data review and collection for model setup using MIKE SHE.
- Began preliminary development of a 1-D stream/river hydrology model using MIKE 11.
- Finishing the literature review for the hydrological modeling and experimental work.

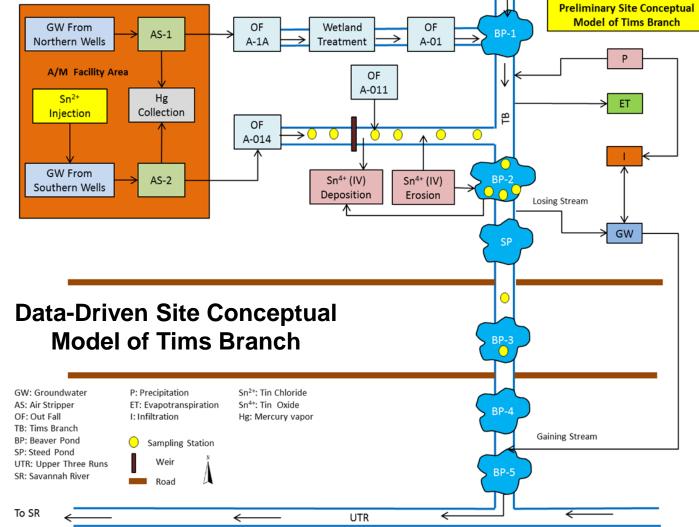


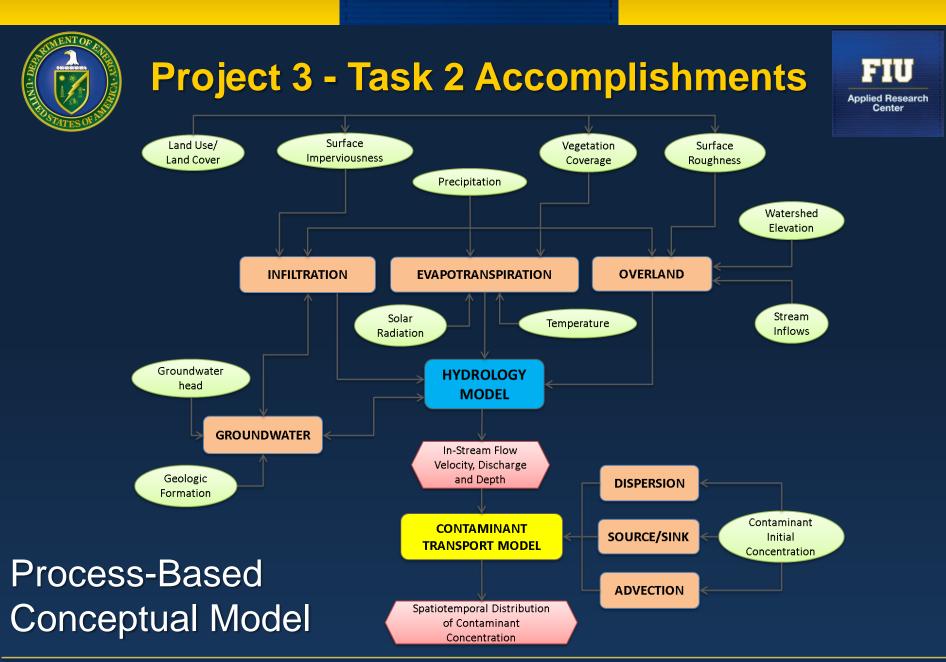




Project 3 - Task 2 Accomplishments

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Task 2: Future Work – FY14 (Year 5)



- Complete Subtask 2.1: Development of detailed GIS-based representation of Tims Branch ecosystem.
- Complete Subtask 2.2: Modeling of surface water and sediment transport in the Tims Branch system.

CLIENT DELIVERABLES	DUE DATE
Technical Report for Task 2: Surface Water Modeling of Tims Branch	6/10/15



Task 3: Description



New Task 3: Sustainability Plan for the A/M Area Groundwater Remediation System

- Supports EM-13 in developing proposed actions for the A/M Area groundwater remediation system infrastructure that will reduce the system's environmental burden.
- Applies analysis and state-of-the-art modeling tools to enable DOE-EM to incorporate sustainability metrics in environmental management decisions.
- Applies to subsurface/surface contamination and supplements traditional risk paradigms to help develop interim and final remediation end-states.
 - Subtask 3.1: Analyze Baseline.
 - Subtask 3.2: Energy Efficiency.
 - Subtask 3.3: Mechanical Design and Operations Modifications for Sustainable Remediation (while controlling contaminant migration)



Task 3: Background

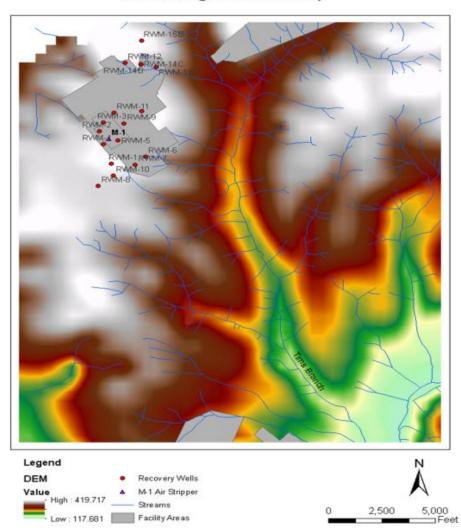


- SRS produced materials for production of nuclear weapons from 1950s-1980s.
- Trichloroethylene (TCE) and tetrachloroethylene (PCE) were main solvents used in degreasing and other industrial operations: Categorized as dense non-aqueous phase liquids (DNAPLs), semi-volatile, and hazardous chemicals.
- 1,600 metric tons of TCE, PCE and 1,1,1-trichloroethane were released into the environment at multiple locations.

SRS A/M Area

- Located in northern part of SRS within lower reaches of Tims Branch watershed (topographic elevation from ~420 ft to ~118 ft).
- Consists of facilities that fabricated reactor fuel and target assemblies (M-Area), and administrative and support facilities (A-Area).





A/M Area Digital Elevation Map

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Task 3: Background



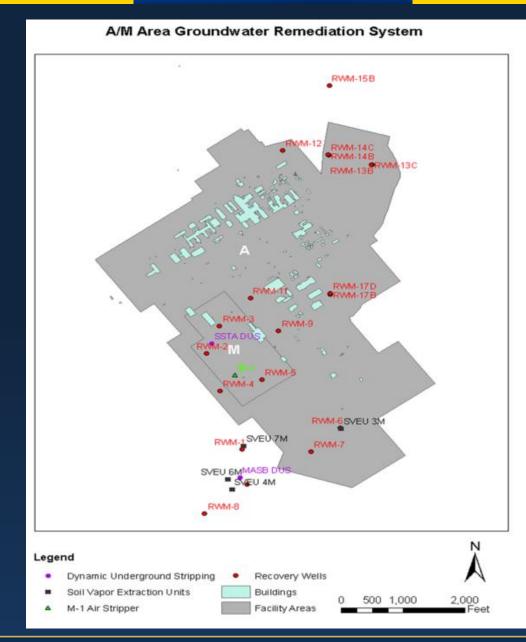
M-1 Air Stripper Performance

- M-1 air stripper and well network operating continuously since 1985 at average electrical load of 150 kW and flow rate of 420 gpm.
- Influent TCE concentration to the air stripper decreased greatly from 25,200 ug/L in 1986 to 2,230 ug/L by end of 2012, with same energy consumption and water pumping rate.

M-1 Air Stripper and Recovery Well Network

- Installed in 1985 to treat groundwater to reduce chlorinated solvent concentrations.
- 17 recovery wells installed over the years. Currently recovery wells 1-12 feed the M1 air stripper.
- Treated groundwater is discharged to a stream in Tims Branch.





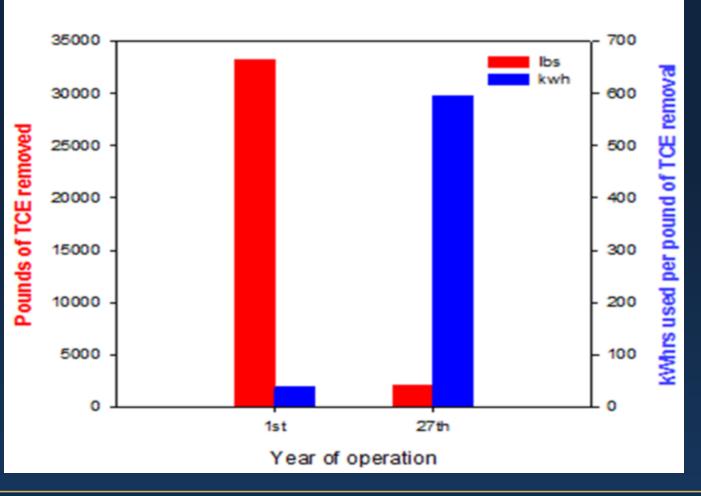
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Task 3: Results



TCE Recovery 1st & 27th Years of Operation

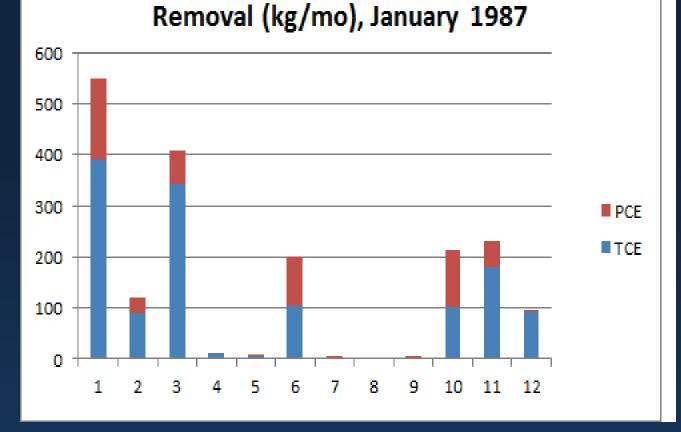




Task 3: Results



TCE & PCE Removal <u>January</u> 1987

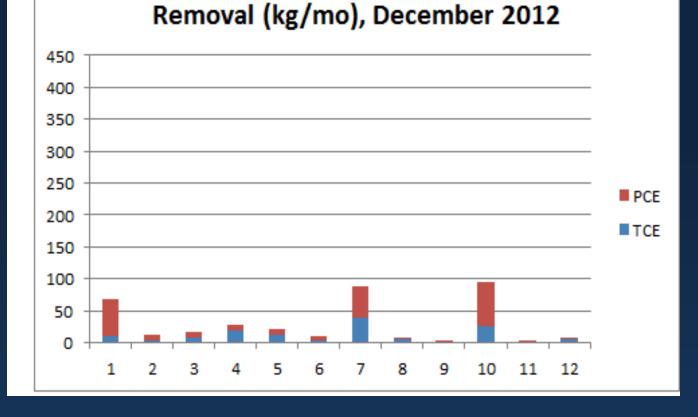




Task 3: Results

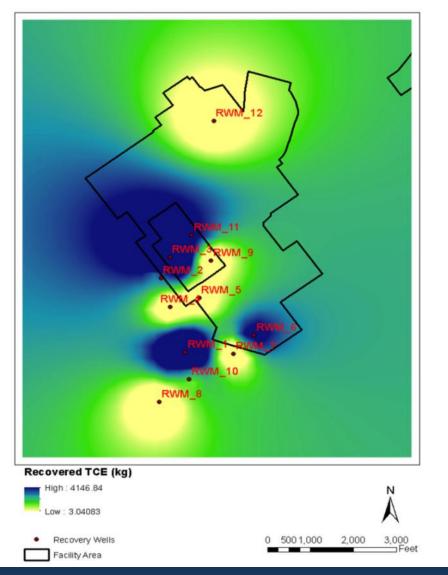


TCE & PCE Removal December 2012





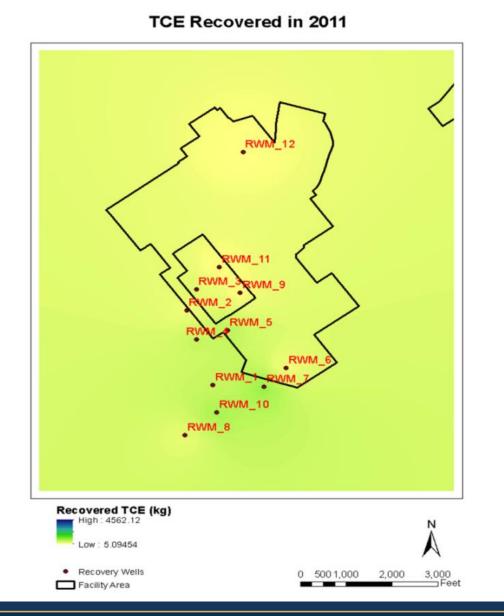
TCE Recovered in 1987



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TCE Recovery in 1987







TCE Recovery in 2011



Task 3: Results



Collection of per Well Data

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

Results per Well

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



Task 3: Results



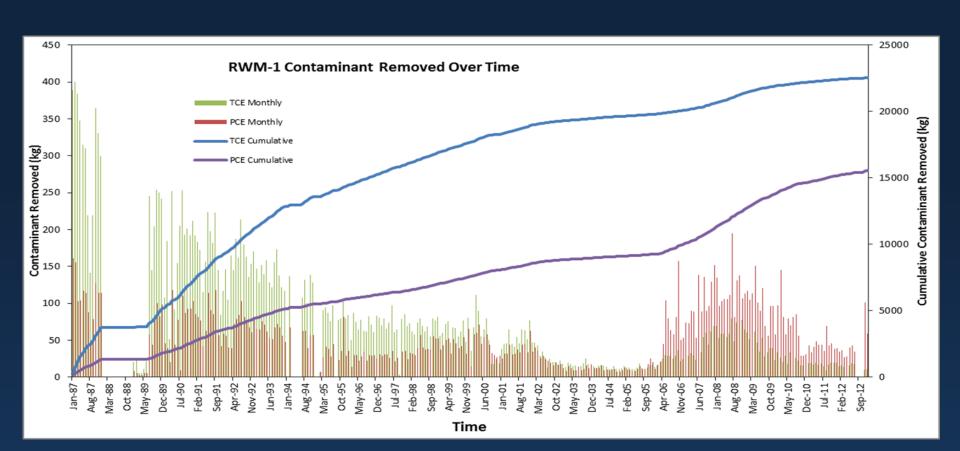
DUS still affecting remediation today

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



Task 3: Results

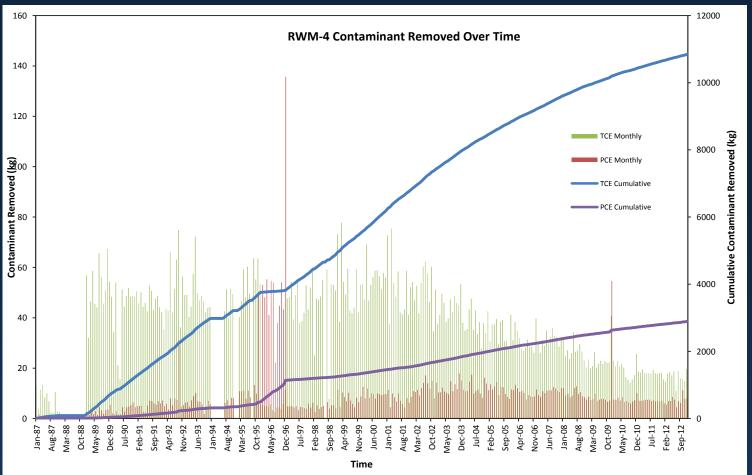






Task 3: Results

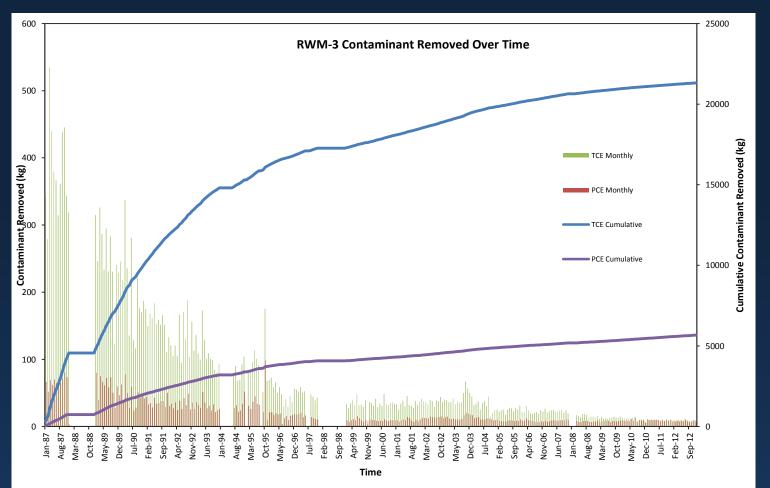






Task 3: Results







Task 3: Results

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Groundwater Concentration Responses (A/M Area Case Study) 25000 r 20000 15000 10000 5000 TCE PCE 1950 2000 2050 2150 2350 2100 2200 2250 2300 Year

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

Source: SRNL Groundwater Concentration in ppb



Project 3 - Task 3 Accomplishments



- Completed and submitted two major Sustainable Remediation reports:
 - "Green and Sustainable Remediation Practices, Tools and their Application at DOE Office of Environmental Management Sites".
 - "Baseline Summary Report for Sustainable Remediation Options for the M1 Air Stripper at DOE SRS" (Subtask 3.1: Analyze Baseline).



M1 Air Stripper at SRS A/M Area



Task 3: Future Work – FY14 (Year 5)



- Identify opportunities to improve efficiencies related to electrical energy, water usage, and the use of other resources, beginning with mechanical design modifications.
- Investigate operational strategies to increase system performance by optimizing the hydraulic loads, pumping rates, contaminant mass flow rates and well drawdown levels.
- Determine a set of metrics which will correlate the pumping rates, the cone of depression, and the interaction between the wells with the contaminant mass flow rates.

CLIENT DELIVERABLES	DUE DATE
Technical Report for Task 3: Sustainability Plan for the A/M Area Groundwater Remediation System	6/17/15



Project-wide: Future Work – FY14 (Year 5)



CLIENT DELIVERABLES	DUE DATE
Presentation overview to DOE HQ/SRNL of the project progress and accomplishments (Year End Review)	6/30/15**
Draft Year End Report	6/30/15*

*Final documents will be submitted to DOE within 30 days of the receipt of comments on the draft documents. **Completion of this deliverable depends on availability of DOE-HQ official(s)





Experimental studies and development/testing of sampling/monitoring technologies for better understanding of long-term behavior of subsurface contaminants and potential effects of remediation technologies.

Proposed research includes:

- Laboratory experiments on soil and contaminants in SRS F/H Area including:
 - Batch and column experiments to estimate adsorption/desorption and transport parameters to better predict and apply remediation technologies.
 - Laboratory analyses of aqueous chemistry of metals (uranium and other radioactive contaminants) in soils and surface water.





Targeted study of contaminants and recovery of Tims Branch may include:

- Biota/biofilm sampling in Tims Branch for contaminants and effects of remediation strategies.
- Laboratory analyses of aqueous chemistry of metals in biota, biofilms, sediments and surface water in Tims Branch including:
 - Laboratory measurements of contaminant concentrations and controlling geochemical parameters (pH, pe, ionic strength, organic carbon, mineralogy, etc.)
 - Measurement of the methylation of tin and mercury in sediments representing the range of conditions present in the SE US.
 - Calculation of chemical thermodynamic coefficients and rates of Hg and Sn methylation in stream and pond sediments.





Development/refinement of surface water models of Tims Branch ecosystem to simulate surface movement, sorption/desorption & transport of contaminants.

- Intercompartmental transfers of contaminants (including water, biota, sediment, biofilm, etc.).
- Sediment trapping of contaminants & associated transport during stormflow.
- Impact geo- and hydro-morphology have on the system and contaminant transport.
- Implementation of transport module to simulate behavior & transport of contaminants in Steed Pond.
- Simulation of current tin (Sn) deposition in stream sediments & future deposition, conc. & transport.
- Modeling of reactive transport of metals (Sn, Hg).
- NOTE: Tims Branch ecosystem is an important applied science opportunity due to significant past research by SREL and SRNL. This collaborative effort is specifically focused on improving conceptual and quantitative modeling of a real-world ecosystem impacted by DOE operations for 50 years and is now recovering. Recently, innovative EM developed treatment technologies that have eliminated anthropogenic mercury sources from this watershed and introduced a known quantity of relatively inert tin oxide tracer.





- Green Sustainable Remediation assessment of the Groundwater Remediation System (GWRS) at A/M Area & other remediation systems/strategies at SRS including:
 - Develop baseline for SRS sustainability performance (water resources, electricity, emissions, etc.) for A/M Area GWRS and propose alternative processes or new technologies to improve sustainability.
 - Work with SRS on follow up studies to facilitate implementation of improved processes/technologies on A/M GWRS.
 - Review additional site remediation systems at SRS, develop baseline, identify improvements with modeling to show impacts and support implementation (one remediation system at a time).





- FIU staff and students will support DOE Office of Soil and Groundwater in the testing and evaluation of ASCEM community released code.
- Based on the DOE Fellow summer internship experience during summer 2014, FIU proposes to involve other DOE Fellows and students in the testing and evaluation of ASCEM code.



Masters & PhDs



- Natalia Duque (DOE Fellow)
 - MS Water Resources EngineeringExpected Graduation Date: Fall 2016



Internships



- Summer 2014
 - Natalia Duque (DOE Fellow)
 - Location: DOE HQ (EM-13), Washington, D.C.
 - Mentor: Albes Gaona, Lead Sustainability Specialist, Office of Deactivation and Decommissioning and Facility Engineering (D&D/FE) (EM-13)
 - Assisted EM with sustainability related projects
 - Developed a Sustainable Remediation Technologies Catalog
 - Researched sustainable approaches to environmental remediation
 - Report Title: "Sustainable Remediation and Literature Review for Savannah River Site A/M Area Groundwater Remediation System"

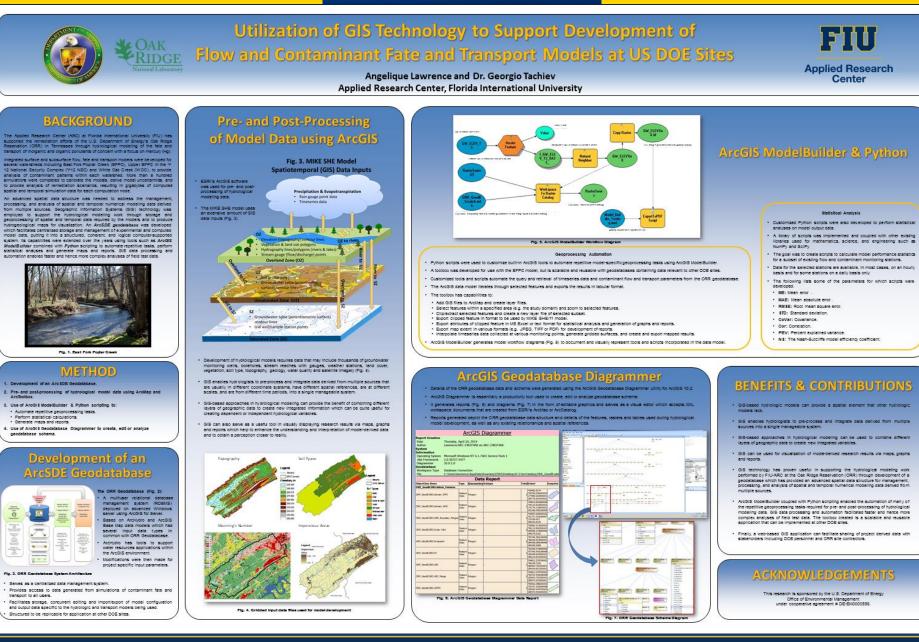


Conferences & Presentations



2015 Waste Management Symposium

- Professional Paper/Poster
 - "Utilization of GIS Technology to Support Development of Flow and Contaminant Fate and Transport Models at US DOE Sites" – Angelique Lawrence, Georgio Tachiev.
- Professional Paper/Presentation
 - "Modeling and Quantitative Assessment of Green and Sustainable Remediation Options for the M1 Air Stripper System at DOE SRS" – David Roelant, Ralph Nichols, Natalia Duque.
- Student Paper/Poster
 - "Column Testing of the Migration and Distribution of Humate Injected into Subsurface Systems at Savannah River Site's F/H Area" – Kiara Pazan (DOE Fellow), Ravi Gudavalli.
 - "Quantitative Assessment of Sustainable Remediation Options for the M-1 Air Stripper System at SRS" – Natalia Duque (DOE Fellow), David Roelant.



Quantitative Assessment of Sustainable Remediation Options for the M-1 Air Stripper System at SRS

Introduction

The US Department of Energy (DOE) Savannah River Site (SRS) covers 310 sq. miles and is located south of Aiken, SC. The site produced materials used in the production of nuclear weapons from the 1950s to the 1980s.

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

In the 1980's, operations were initiated to remediate the contaminated soil and groundwater which continues today.

Problem Statement

The M-1 air stripper and well network has operated continuously since 1985 at an average electrical load of 150 kW and flow rate of 420 gpm. The influent TCE concentration to the air stripper has decreased exponentially from 25,200 ug/L in 1986 to 2,230 ug/L by the end of 2012, with the same energy consumption and water pumping rate.

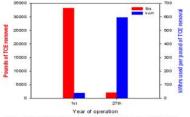


Figure 1: M-1 Stripper TCE removal During 1# and 27th Year of Operation

Purpose

To analyze the operation of the SRS A/M Area groundwater remediation system using state-of-the-art modeling tools to provide suggested engineering and operational improvements to expend less resources while still containing the contaminant plume.

Implementation of improvements will help DOE-EM apply sustainable remediation at its sites and help DOE achieve DOE-wide sustainability performance metrics.

A/M Area

- Located in the northern part of SRS within the lower reaches of the Tims Branch watershed (topographic
- elevation from ~420 ftto ~ 118 ft).
 Consists of facilities that fabricated reactor fuel and target assemblies (M-Area), and administrative and support facilities (A-Area).

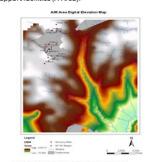


Figure 2: SRS A/M Area Digital Elevation Map

- M-1 Air Stripper & Recovery Well Network
- Installed in 1985 to treat groundwater in order to reduce chlorinated solvent concentrations.
- 17 recovery wells have been installed over the years. Currently recovery wells 1-12 feed the M1 air stripper.
 The treated groundwater is discharged to a stream in



RS A/M Area Remediation Net

Preliminary Results

The monthly removal rate and the cumulative mass removed for TCE and PCE in the 12 recovery wells was analyzed for 1985-2012. Removal from well RWM-1 is plotted below.

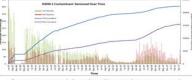


Figure 4: RWM-1 Cumulative and Monthly TCE and PCE Mass Removed

- 7 of 12 recovery wells have transitioned to more PCE than TCE removed. This is an expected result since TCE was initially used and then replaced by PCE.
- The rate of recovery in some wells was affected by the Dynamic Underground Stripping process.
- 7 wells exhibit exponential decay in contaminant removal while 5 exhibit steady concentrations, and 2 exhibit linear decreases.

Table 1: Comparison of Contaminant Removal 1987 to 2012

Well		TCE				PCE			
ID RWM	Jan. '87 removal (kg/mo.)	Dec. '12 removal (kg/mo.)	Jan. '87 H ₁ O Intensity, kg/Mgal	Dec. '12 H ₂ O Intensity, kg/Mgal	Jan. '87 removal (kg/mo.)	Dec. '12 removal (kg/mo.)	Jan. '87 H ₂ O Intensity, kg/Mgal	Dec. '12 H ₂ O Intensity kg/Mgal	
1	389.00	10.57	243	26.9	161.35	58.76	101	149	
2	89.09	3.00	98.2	3.24	29.43	8.68	32.4	9.39	
3	341.37	8.94	116	3.89	66.55	7.53	22.7	3.27	
11	180.52	2.18	69.6	.931	49.59	0.16	19.1	0.0665	
4	12.96	19.64	23.1	10.0	0.00	8.13	0.00783	4.15	
5	5.29	13.35	5.32	6.57	1.43	8.26	1.44	4.07	
7	3.48	40.15	7.32	23.8	2.90	48.72	6.10	28.9	
8	0.09	5.20	0.129	2.66	0.22	3.67	0.305	1.88	
10	101.16	24.89	52.0	18.5	111.05	70.67	\$7.1	52.4	
6	105.00	2.90	73.7	2.70	95.94	7.58	67.3	7.04	
12	91.76	6.39	39.3	3.11	0.05	0.06	0.0196	0.03.13	
9	3.77	1.73	3.23	9.085-07	0.67	0.53	.571	.278	

Future Work

- Identify opportunities to improve efficiencies related to electrical energy, water usage, and the use of
 other resources, beginning with mechanical design modifications.
- Investigate operational strategies to increase system performance by optimizing the hydraulic loads, pumping rates, contaminant massflow rates and well drawdown levels.
- Determine a set of metrics which will correlate the pumping rates, the cone of depression, and the
 interaction between the wells with the contaminant mass flow rates.

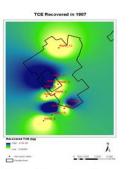


Figure 5: TCE (kg) Recovered per Well in 1987.

Applied Research Center



Natalia Duque (DOE Fellow)



Figure 6: TCE (kg) Recovered per Well in 2011.

Workforce Development Program Florida International University, Applied Research Center (FIU-ARC): Dr. David Roelant

DOE-FIU Science and Technology

Ms. Angelique Lawrence Dr. Leonel Lagos

Acknowledgments:

DOE EM-13: Mr. Albes Gaona

Results

Column Testing of the Migration and Distribution of Humate Injected into Subsurface Systems at Savannah River Site's F/H Area

Kiara Pazan (DOE Fellow), Dr. Ravi Gudavalli (Mentor)

Applied Research Center, Florida International University

Background

- Remediation by humic acid (HA) has shown to be a





Humate Injecte

Fig 1. Area seepage basins (from Fig 2. Co Millings et al., 2013). H

Objectives

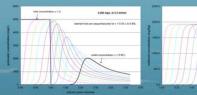
- Study the migration and distribution of HA injected in to subsurface systems by column experiments in support of uranium remediation.
- > Obtain sorption and desorption parameters and understand sorption under different levels Hato

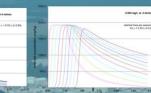
Methodology

- Characterization of F-area soil.
- Perform column flow through bromide tracer tests. Preparation of artificial groundwater to mimic SRS
- groundwater.
- Preconditioning of columns to bring pH of soil to field conditions.
- pH of 3.5, 5.0, 6.0, 7.0 will be attained.
- Injection of Huma-K into column and study the sorption by analyzing the effluent via UV-Vis spectrophotometer.
- Perform desorption for 3.5, 5, 6, and 7 pH solutions.

- Soil Characterization: FAW-160'-70'
 - Bulk density: 1.334 g/cm³
- Porosity: 0.496 > pHw:4.06
- Humate Injection scenarios are used to predict the sorption of HA on sediment and determine optimum concentration of Huma-K and flow rate, as well as to compare to experimental breakthrough curves.
 - iection Scenarios
 - a: 2082 mg/kg
 - b: 0.0025 L/mg
 - Cell pore vol/time step: 0.4 Huma-K Concn: 5000 mg/L





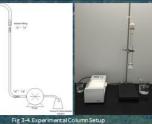


1.000 mpl, at 2.5 millio

Fig 5-8 Simple conceptual models of humate injection using Lang isotherm

Discussion

- The injected Huma-K at high pH is expected to decrease the mobility of organic molecules as pH decreases, as it interacts with the soil and flushing of artificial groundwater. Flushing of artificial groundwater.
 The expected results should demonstrate that humate sorbed to soil should bind with uranium at acidic pH.
- The modeled injection scenarios suggests the optimal Huma-K concentration and flow for columns should be 5000 mg/L at 2.5 ml/min, avoiding over saturation and best amount of sorption to sediment.
- The results from previously conducted humate injection tests will be used to compare the properties of humic acid.



- **Future Work**
- Continue column experiments to determine sorption and desorption properties to use for actual field deployment
- In addition to uranium, ICP tests will be performed for iron and silica.
- Data from this experiment will be used to develop a subsurface flow, rate, and transport model of distribution of humic acid for in situ treatment



Abstract

The F-Area seepage basins at Savannah River Site (SRS) have received approximately 1.8 billion gallons of lowlevel waste solutions, containing nitric acid, radionuclides and dissolved metals due to plutonium separation operations from 1955 to 1988. The waste solutions became a source of contamination for groundwater and soil at the site, with U(VI) and other radionuclides above their maximum contaminant levels (MCLs). For remediation, humic acid (HA) technology has shown to be a potential approach for controlling mobility of radionuclides. Because sorbed HA and uranium develop a strong bond at slightly acidic pH, the mobility of the contaminant molecules should decrease with flushing of SRS groundwater. Column experiments are planned using SRS soil from the F/H Area to examine the sorption and desorption properties of HA in SRS soil. The data from these experiments will then be used to perform modeling of the migration and distribution of HA injected into the subsurface.

Acknowledgements

- Dr. Leonel Lagos
- Dr. Miles Denham
- DOE-FIU Science & Technology Workforce Development Program





QUESTIONS

FLORIDA INTERNATIONAL UNIVERSITY

