



Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

DOE-EM Cooperative Agreement – Year 3 Research Review Project 3: Remediation and Treatment Technology Development

Presented: April 30, 2013
to the U.S. Department of Energy
by Georgio Tachiev, Ph.D., P.E.
Angelique Lawrence, Amy Cook

*Worlds
Ahead*

Advancing the research and academic mission of Florida International University.



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Vadim Katsenovich (undergraduate), Stephanie Sierra



Project Description

General Objective:

- “ Provide technical assistance and perform research in support of the remediation and treatment technology development at ORR and MOAB

Work Scope:

- “ Develop integrated surface/subsurface flow and transport models of EFPC and WOC watersheds
- “ Develop a geodatabase for data storage, access, and retrieval using automated data processing
- “ Optimize the operation of groundwater extraction well fields, infiltration of treated water, and injection of clean water for UMTRA site in Moab, Utah
- “ Use developed hydrological model to:
 - “ Analyze contaminant transport patterns
 - “ Simulate hydrologic events and determine their effect on contaminant transport within the watershed
 - “ Determine hydrological and transport parameters with greatest impact TMDL
 - “ Predict effects of proposed remediation activities on TMDL, transport patterns, and fluxes
 - “ Evaluate risks during D&D
- “ Perform laboratory experiments to obtain more information on significant parameters related to Hg transport, reaction, and speciation within the watershed (e.g., methylation/demethylation kinetics)

The most cost effective and successful cleanup of contaminant streams, soil, and groundwater within EFPC will be achieved with a better understanding the physiochemical characteristics of mercury and the impact of hydrology on mercury cycling and transport. Our project work provides a tool for understanding the impact of selected remediation scenarios on water and mercury fluxes across ORR.



Project Accomplishments of 2012-2013

- “ Provided training for 5 DOE Fellows
- “ Provided 5 student internships
- “ Published 4 journal articles
- “ 2 consecutive “Best Professional Poster” awards at the WMS (2012 and 2013)
- “ Completed 5 MS theses
- “ 2 PhDs in progress
- “ Presented 4 posters and 1 paper at WM 2013



Overview of Project Tasks

“ Task 1: EFPC Model Update, Calibration, Uncertainty Analysis

- Extend water quality and sedimentation module for entire EFPC; provide sensitivity analysis and determine model uncertainty; implement sedimentation module in creek water and overland. (*Models derived in terms of total mercury*).
- Create detailed surface water flow and contaminant transport model for ORNL area using XPSWMM; incorporate flow and other significant drainage system parameters. Benchmark study to be extended to Y-12 NSC.

“ Task 2: TMDL Analysis for EFPC

- Provide water body characterization; determine loads and conduct load duration curve analysis; provide water balance; determine surface and subsurface transport patterns; quantify exchange between surface and subsurface; determine mass balance of total mercury in water, soil, sediments and pore water.

“ Task 3: Parameterization of Major Transport Processes of Mercury Species

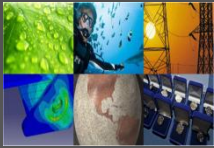
- Extend the work on the stability, mobility, and reactivity of the aged mercury species in soils and sediments using comparative studies of theoretical and experimental work; Examine effects of thiol-containing substances and other environmental factors on dissolution of mercury sulfide (cinnabar); Examine effects of environmental factors on key mercury transformation processes (e..g, demethylation).

“ Task 4: Geodatabase Development for Hydrological Modeling Support

- Extend capabilities of EFPC geodatabase developed in FY11 using ArcGIS ModelBuilder and Python scripting to automate query and export of hydrological modeling data for statistical analysis and the generation of maps, graphs and reports; Investigate downloadable free/open source GIS software for online querying of geodatabase.

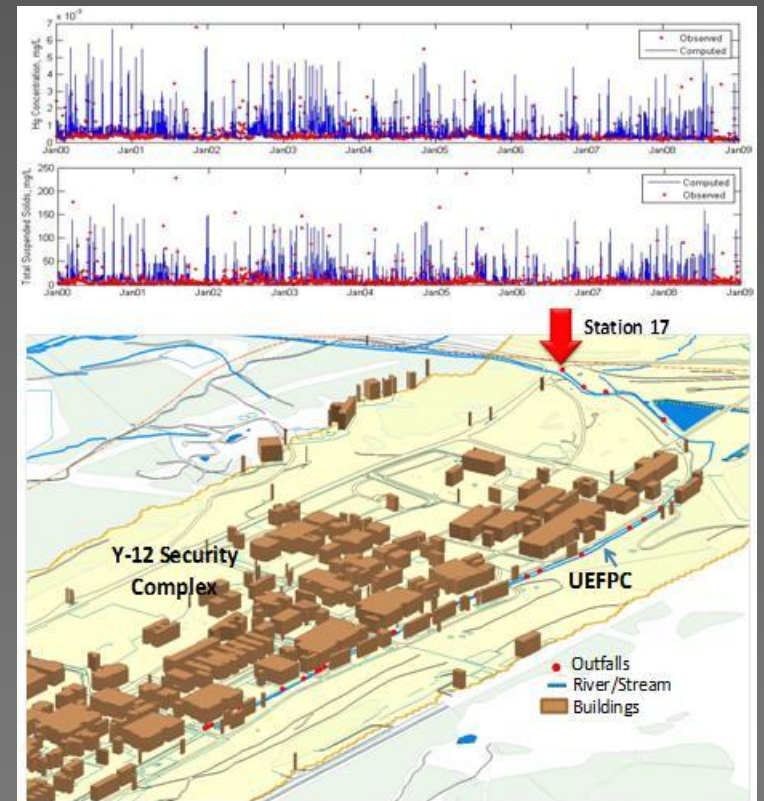
“ Task 5: Student Support for Modeling of Groundwater Flow and Transport at the Moab Site

- Model update and improvement; model calibration and validation, prediction and sensitivity analysis.



Task 1: EFPC Model Update, Calibration, Uncertainty Analysis

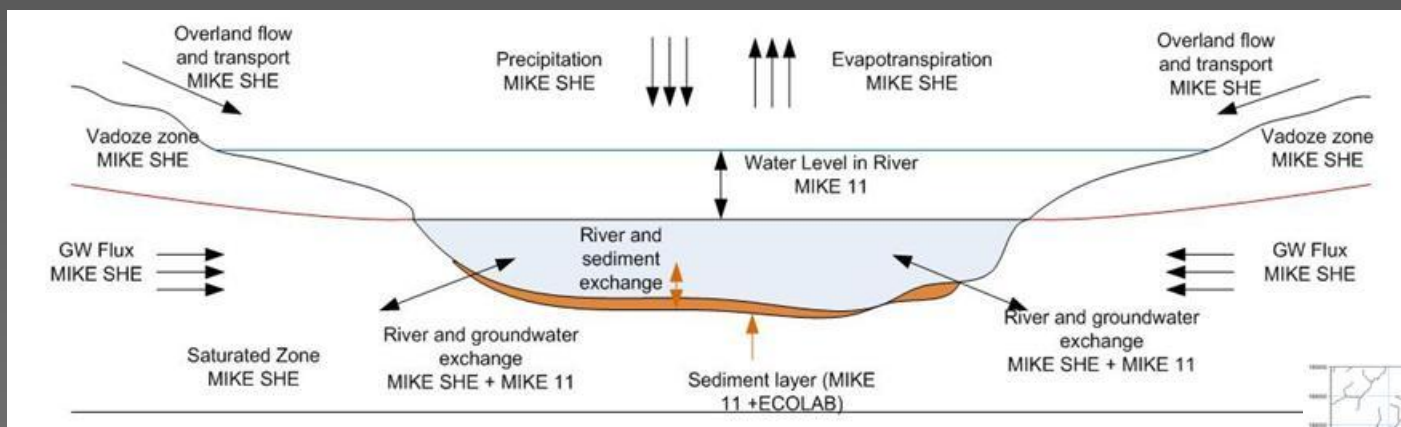
- “ Implemented sedimentation module and included 52 additional outfalls covering the entire EFPC and Bear Creek watersheds.
- “ Performed numerical simulations using a range of Manning’s numbers, threshold run-off water depths, and drainage coefficients for calibration of flow (2000–2008).
- “ Developed MATLAB scripts for statistical analysis of model results.
- “ Analyzed simulations using comparative schematics of timeseries plots, probability exceedance curves, and load duration curves.
- “ Provided assessment reports on the effectiveness of 8 different remedial scenarios.



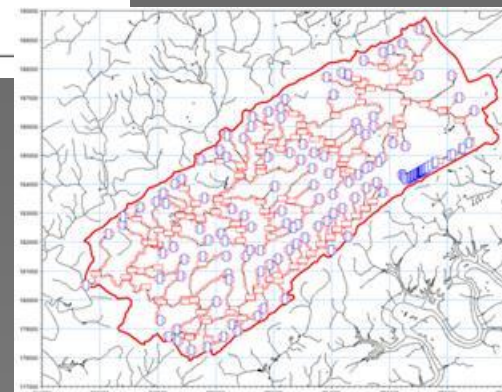
Total suspended solids and Hg concentration compared with historical data at Station 17



Task 1: EFPC Model Update, Calibration, Uncertainty Analysis



Extended the existing hydrological 2D model of the domain (MIKE SHE) and 1D model of rivers (M11) with an ECOLAB module to provide ecological modeling and simulate the fate and transport of mercury at the water and sediment interface along East Fork Poplar Creek and determine the reactive flow and the exchange between sediments and river

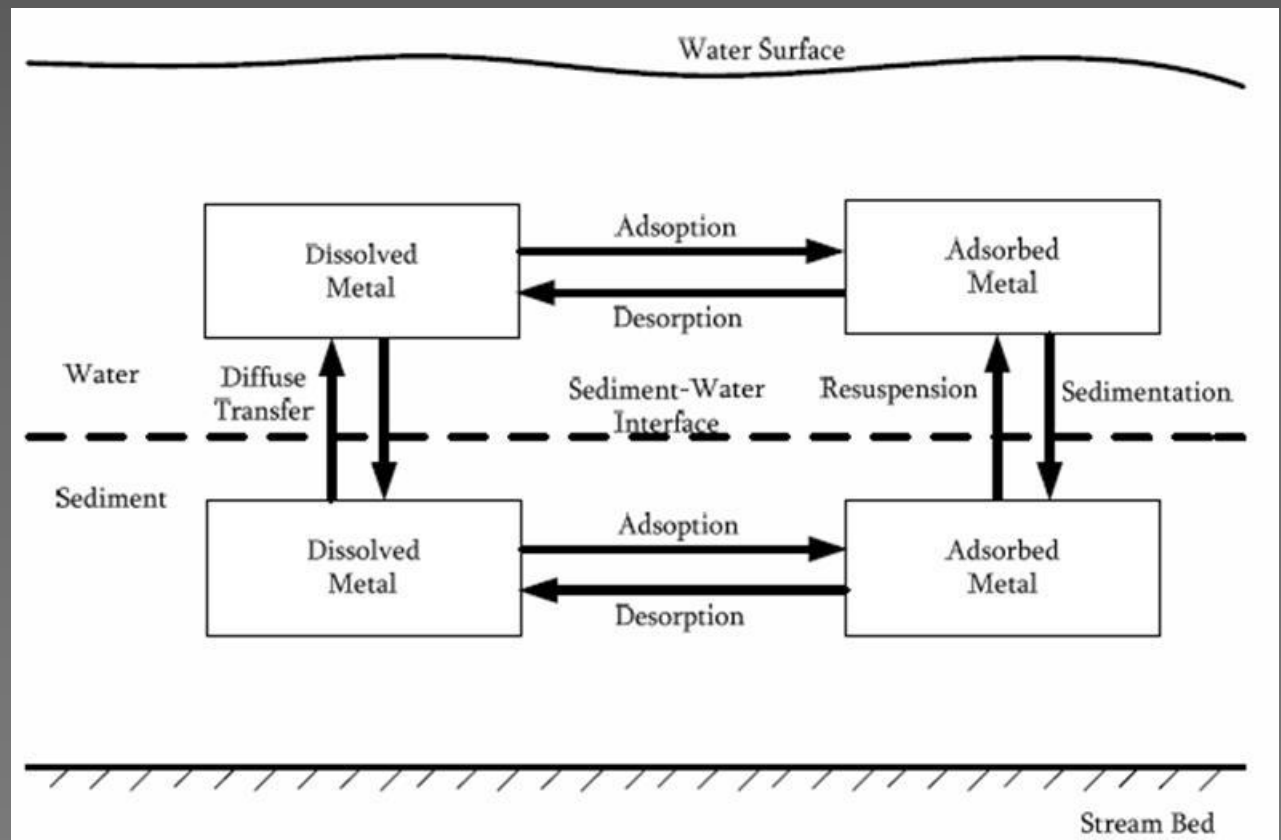


River network with point nodes, boundary conditions and cross-sections links.



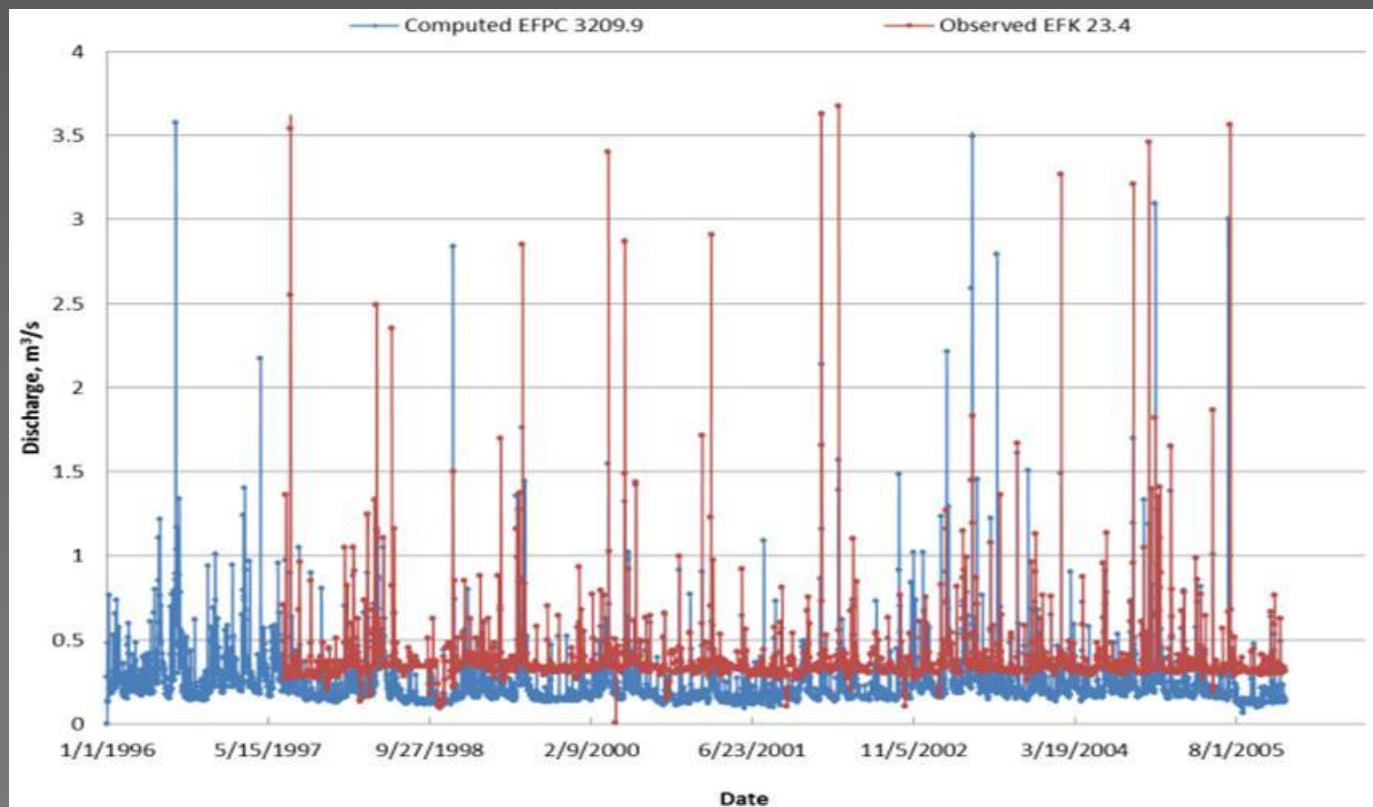
Task 1: EFPC Model Update, Calibration, Uncertainty Analysis

- “ Provided simulation of contaminant fate and transport based on planned remediation scenarios. (Hg, PCE, TCE, 1,2-DCE, cis-1,2-DCE, and VC).
- “ Predicted plume migration and possible exceedances of risk/hazard-based concentrations. Computed data is utilized for TMDL calculations.





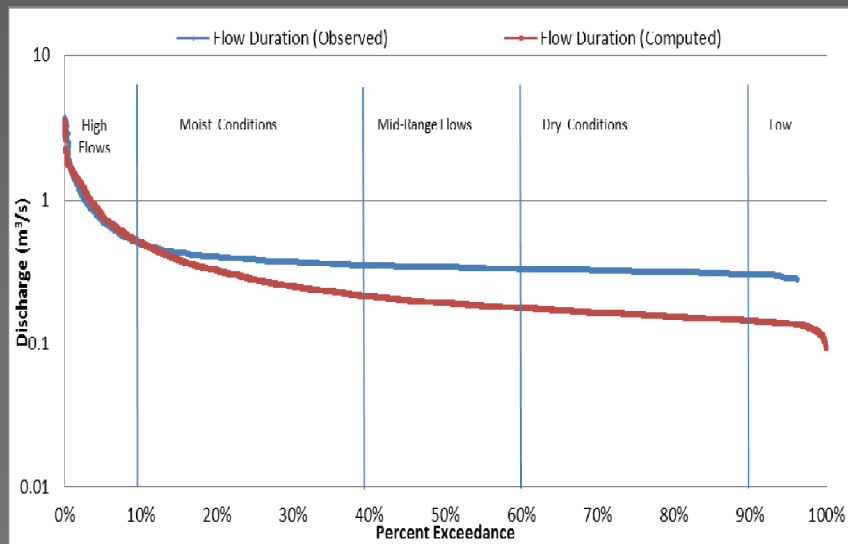
Task 1: EFPC Model Update, Calibration, Uncertainty Analysis



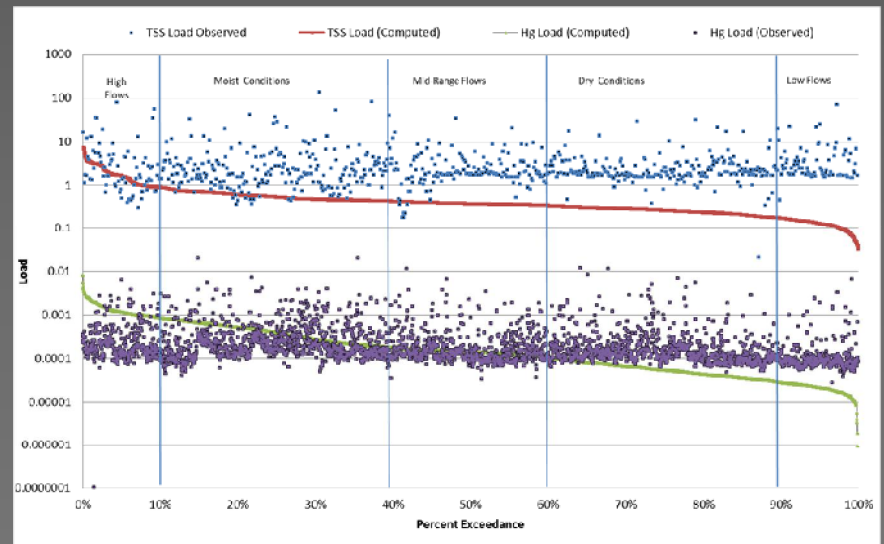
AN example of comparison of discharge timeseries
EFPC computed (blue) and observed at EFK 23.4 (red)



Task 1: EFPC Model Update, Calibration, Uncertainty Analysis



Comparison of flow duration curves for EFPC 3209.9 (red) and EFK 23.4 (blue)

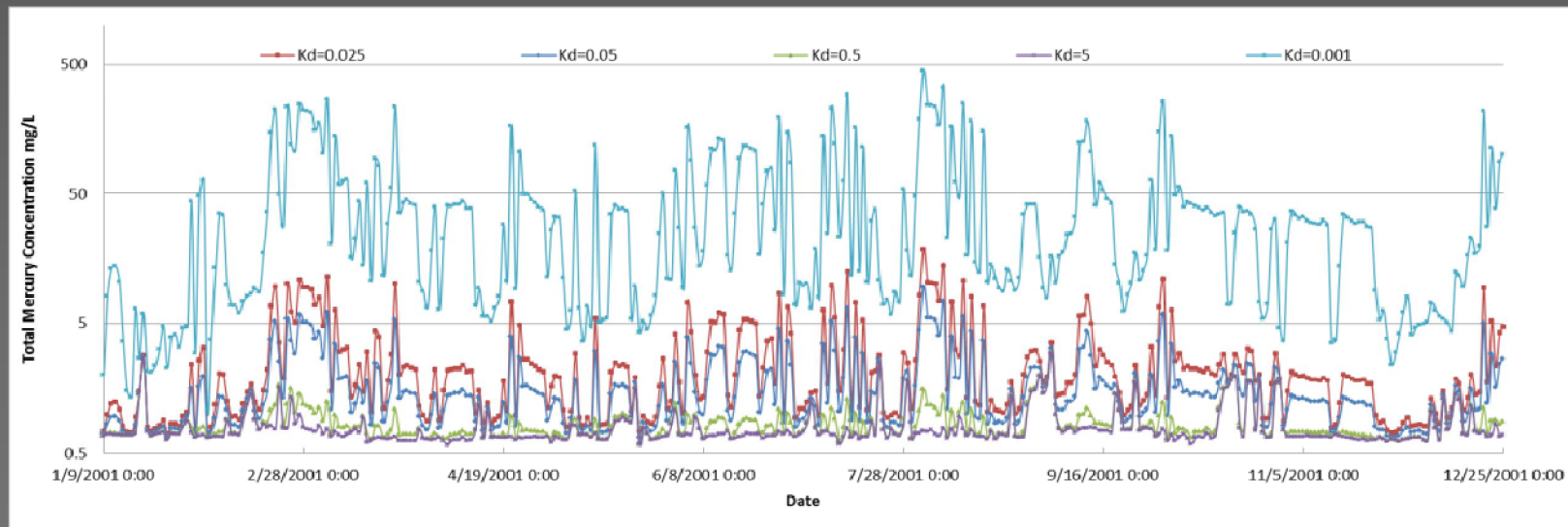


TSS load observed (blue dots) and computed (red line) and mercury concentration load observed (purple dots) and computed (green line) for Station 17

Analysis conducted through probability exceedance and duration curves (flow, concentrations and load)



Task 1: EFPC Model Update, Calibration, Uncertainty Analysis



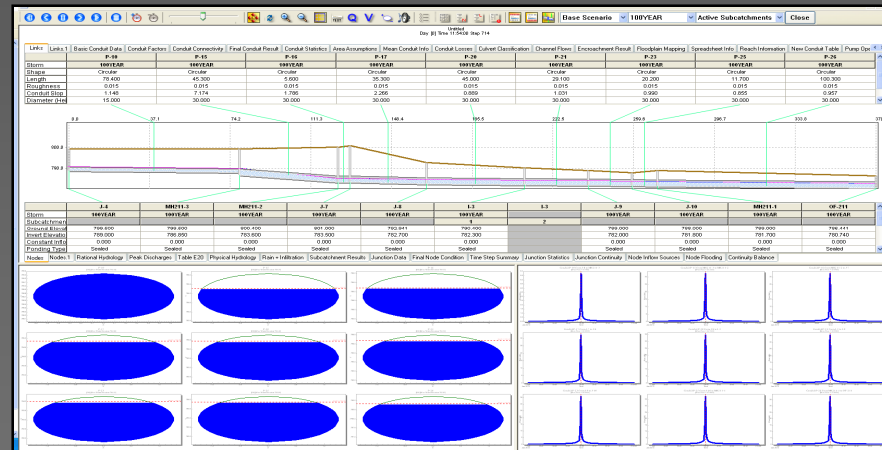
An example of computed total mercury timeseries depicting sensitivity to organic partition coefficient (K_d) for $K_d=0.025$ (red), $K_d=0.05$ (blue), $K_d=0.5$ (green), $K_d=5$ (purple), and $K_d=0.001$ (teal)

Task 1: EFPC Model Update, Calibration, Uncertainty Analysis

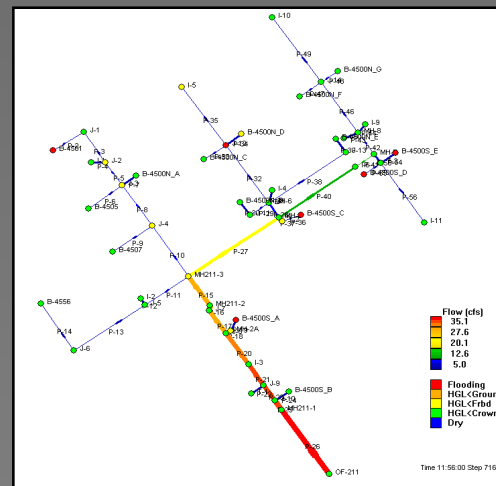
- Created surface water flow and contaminant transport model for contributing drainage areas to Outfall 211 of ORNL Area using XPSWMM, incorporating flow and other significant drainage system parameters.
- Model demonstrated to be effective tool by its response to rainfall data during calibration.
- Sensitivity analysis proved model sensitive to various Manning's roughness coefficients, infiltration parameters, and adjusted imperviousness of the sub-catchment areas; however, not enough to alter the flow rates in the system.
- Transport analysis has provided insight into how a conservative contaminant would react within the system if introduced at various locations.



Outfall 211



XPSWMM 100-Year 24-Hour Storm Event

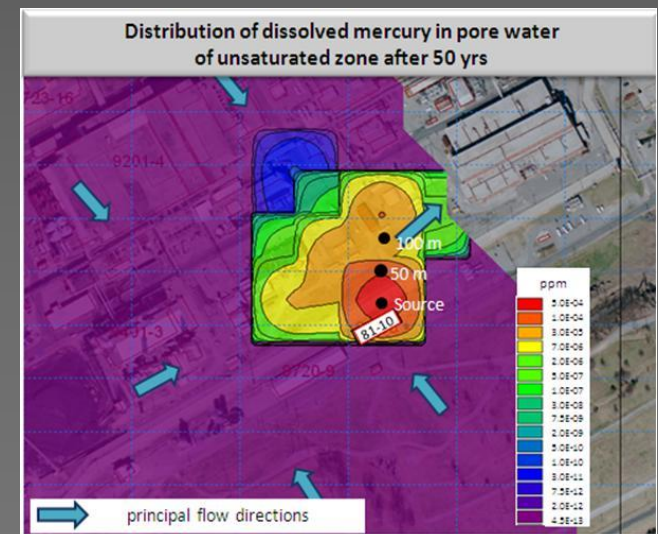


XPSWMM 100-Year 24-Hour Storm Event Areas of Flooding



Task 2: TMDL Analysis for EFPC

- “ Updated field & lab data related to water quantity & quality extracted from OREIS
- “ Identified data gaps and data needs and monitoring recommendations
- “ Performed spatial & temporal analyses to identify spatial variations of Hg in EFPC water, shallow & deep soil layers, stream bank & streambed sediments and evaluate timing of impairment, potential source loading or other conditions contributing to impairment.
- “ Did review and analysis of NPDES and TMDL requirements (literature review) for EFPC established by EPA and TDEC.
- “ Conducted NPDES and TMDL analysis of the entire EFPC.
 - . Target mercury concentration for the EFPC was determined based on TDEC regulations for surface waters.
 - . Load and flow duration curves were graphed for the outfalls and compared with simulation results.
 - . Submitted progress report in February 2012 entitled “Simulation of TMDL for the Entire EFPC” which includes information on NPDES and TMDL target definition, development of flow and load duration curves and load allocation analysis.

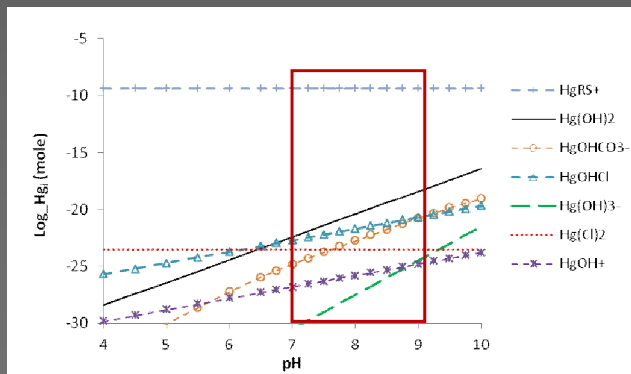


Predicted Hg concentrations in all cases do not exceed risk-based target groundwater concentration of 0.036 mg/L for industrial use scenario.



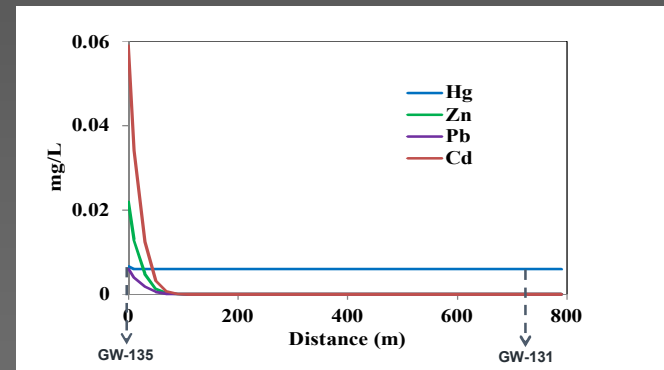
Task 2: TMDL Analysis for EFPC

- “ Develop the Hg Thermodynamic Data for EFPC
- “ Assessed the capability of PHREEQC to simulate the Hg species distribution in EFPC water

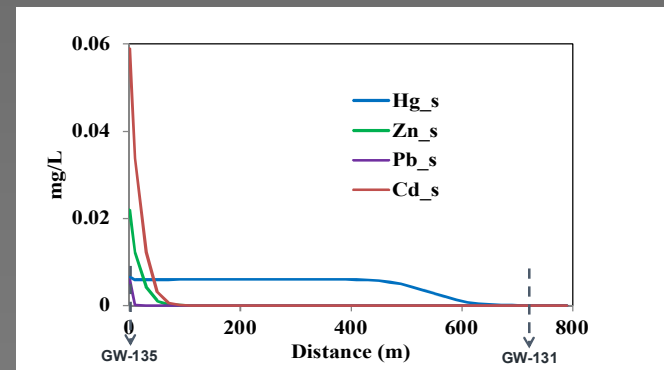


Hg species distribution in EFPC water

- “ Tested two hypotheses of metal transport in the Ca-Mg-HCO₃ groundwater water, as influenced by
 - “ the role of ion exchange and
 - “ the role of both ion exchange and sorption, the latter via surface complexation with Fe(OH)₃



Transport of Hg in groundwater at Y-12 plant with role of ion exchange



Transport of Hg in groundwater at Y-12 plant with role of ion exchange and sorption on Fe(OH)₃

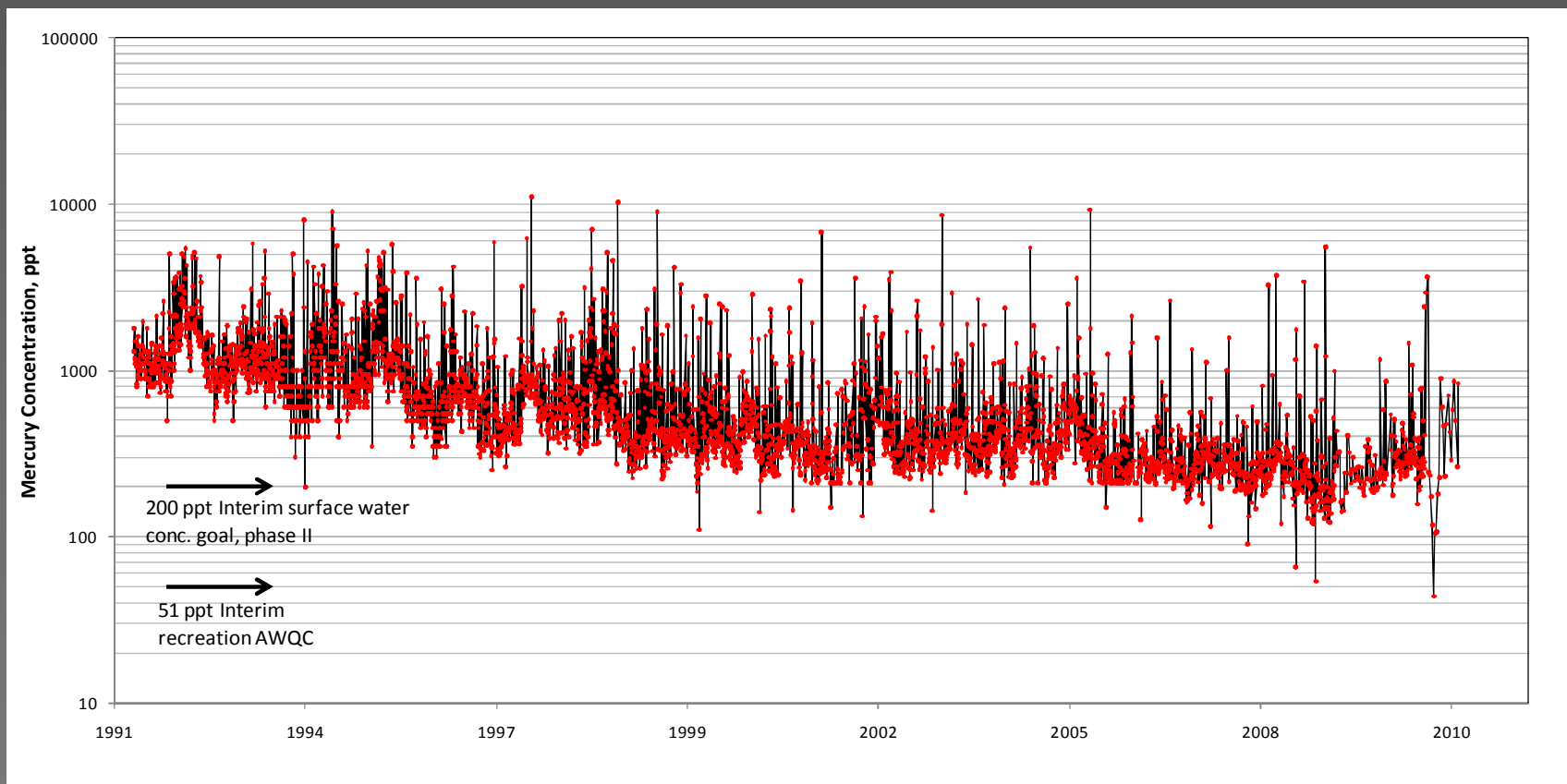


Task 2: TMDL Analysis for EFPC

- “ Groundwater/surface water modeling was used to determine efficacy of stabilization in place (SIP) with hydrologic isolation for remediation of mercury contaminated areas in the Upper East Fork Poplar Creek (UEFPC) Watershed in Oak Ridge, TN.
- “ SIP alternative could be less expensive than excavation, treatment, and disposal of mercury contaminated soil/sediment.
- “ Modeling conducted on watershed scale used to determine effect of removal of mercury contaminated soil sources on surface water concentrations at Station 17, a surface water integration point.
- “ Modeling conducted on local scale to determine transport in groundwater from former Building 81-10 area, a site with a liquid elemental mercury in soil.



Task 2: TMDL Analysis for EFPC

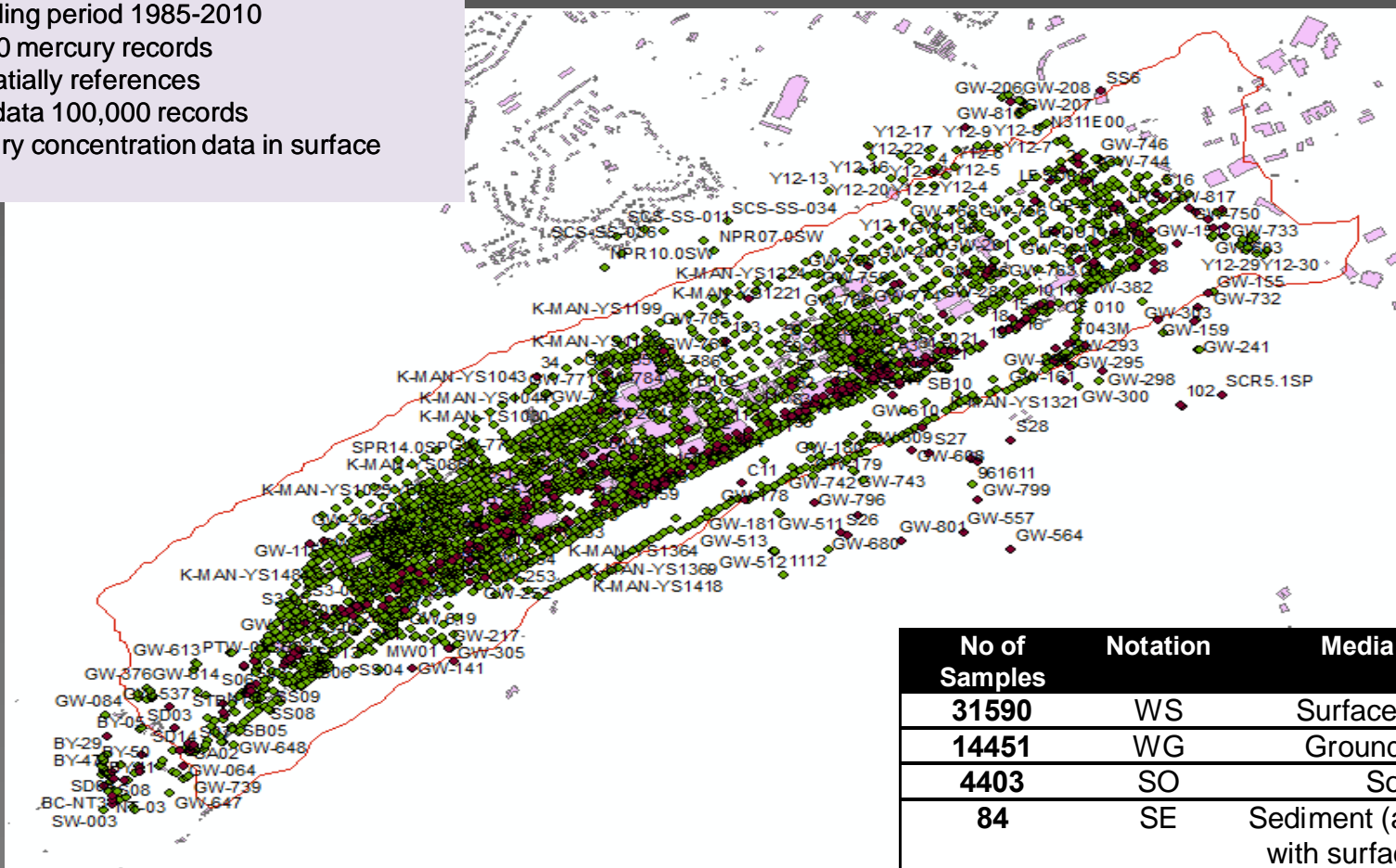


Mercury Concentration in UEFPC at Station 17 Relative to Interim Goals



Task 2: TMDL Analysis for EFPC

- “ Sampling period 1985-2010
- “ 54,000 mercury records
- “ All spatially references
- “ Flow data 100,000 records
- “ Mercury concentration data in surface water

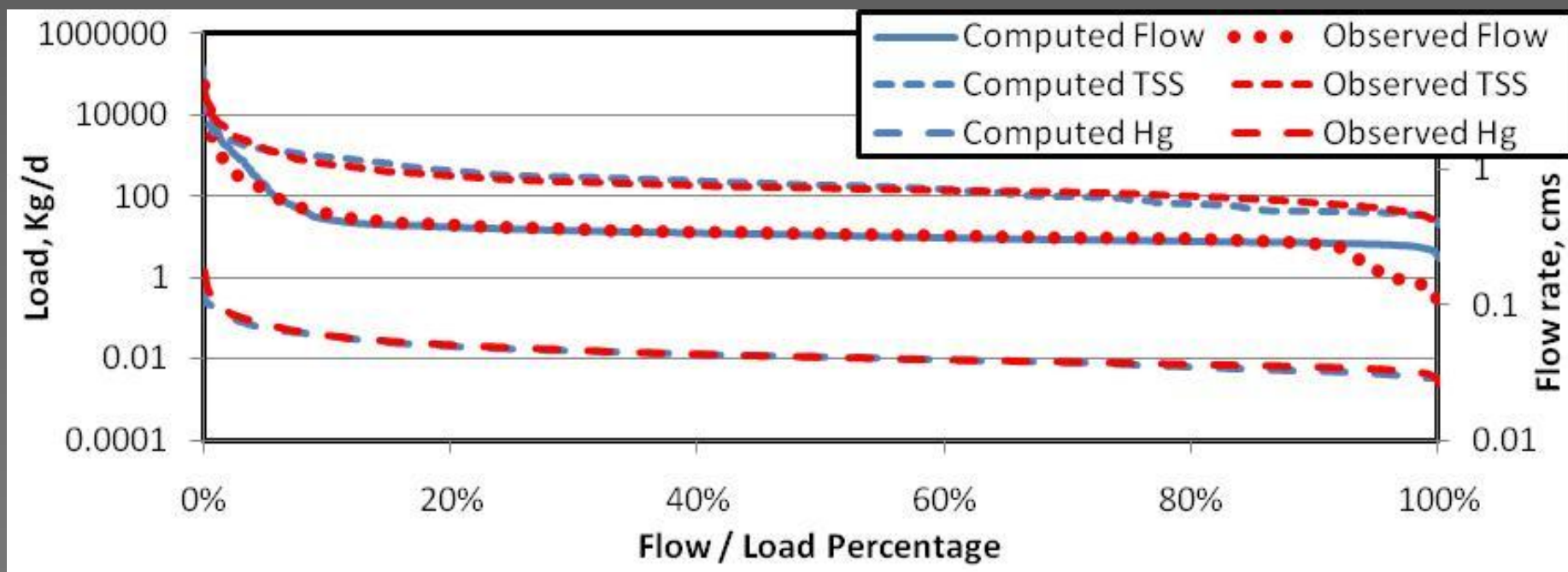


OREIS Database (Query: Oct 2010)

Mercury Concentrations in Soil in the Watershed Model Domain



Task 2: TMDL Analysis for EFPC

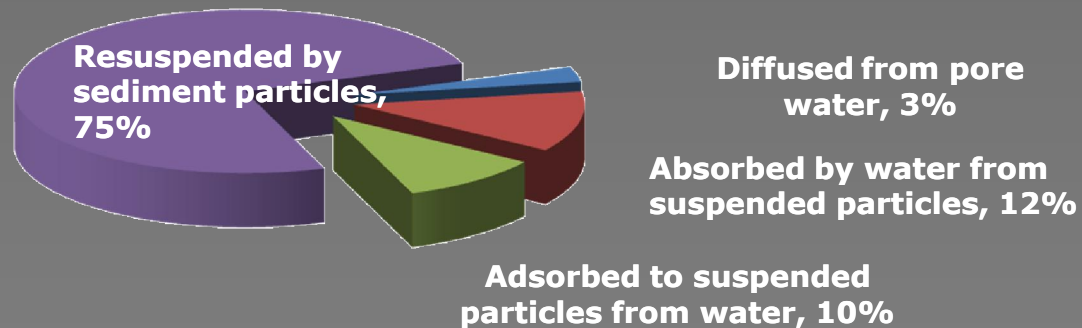


Computed VS Observed Flow, TSS, and Hg Load (Flux) Duration Curves at Station 17



Task 2: TMDL Analysis for EFPC

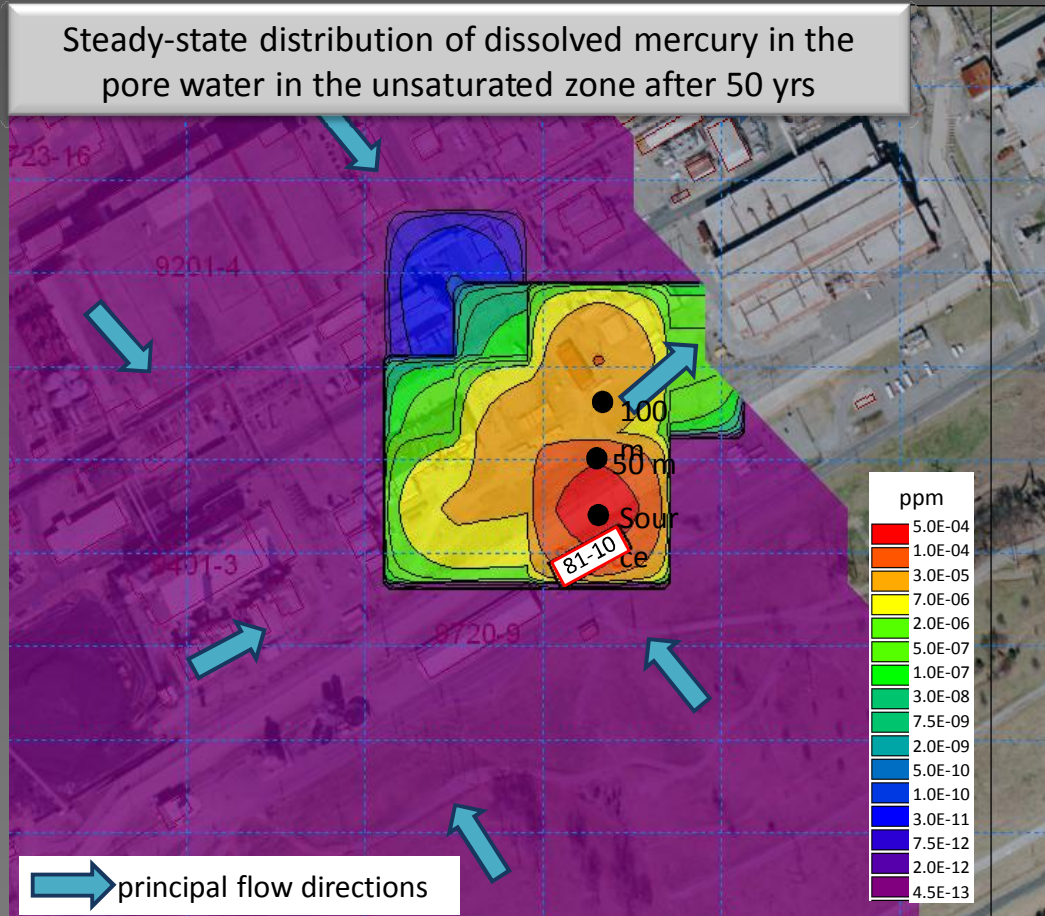
- “ The major mode of mercury transport within the watershed is through mobilization by surface water. Colloidal transport contributed more than 85% of the total mercury flux leaving the Upper East Fork Poplar Creek watershed. This may cause most of the mercury flux under high flow conditions.
- “ Mercury in the soil and sediment source areas adjacent to the stream and in sediment that is eroding can contribute to the flux of mercury at Station 17. Because colloidal mercury could be transported in surface water, actions that trap colloids and or hydrologically isolate surface water runoff from source areas would reduce the flux of mercury at Station 17.



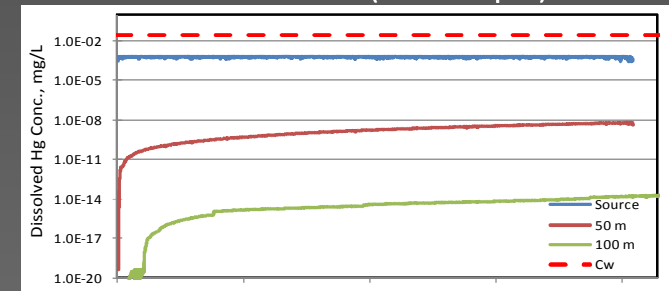


Task 2: TMDL Analysis for EFPC

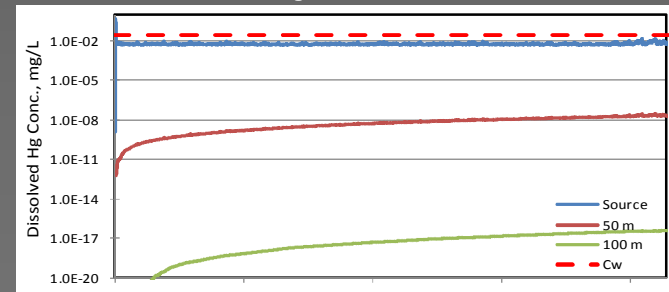
Steady-state distribution of dissolved mercury in the pore water in the unsaturated zone after 50 yrs



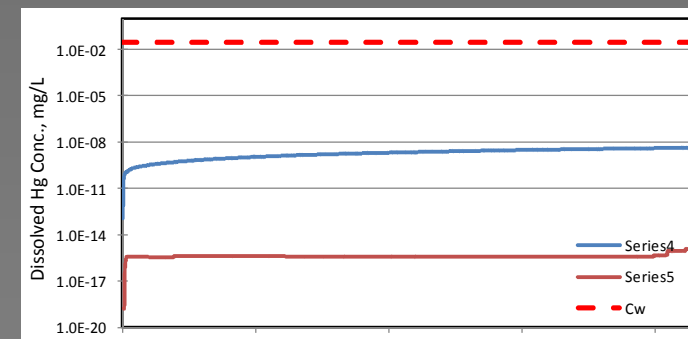
Unsaturated Zone (0 to 3 depth)



0.036 mg/L industrial use risk factor

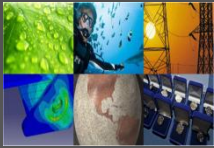


0.036 mg/L industrial use risk factor

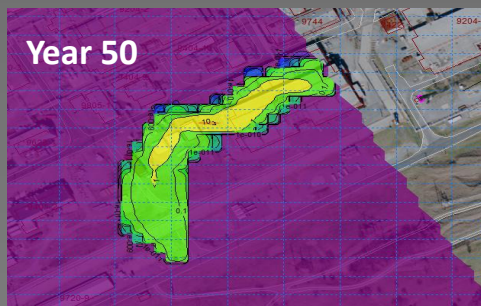
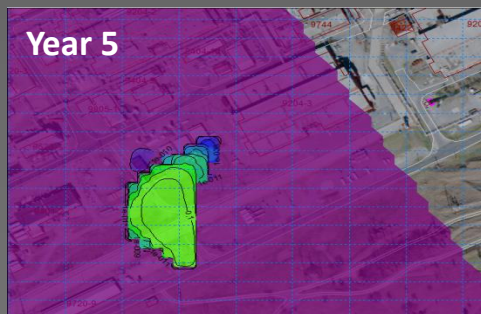


12/27/1979 12/24/1989 12/22/1999

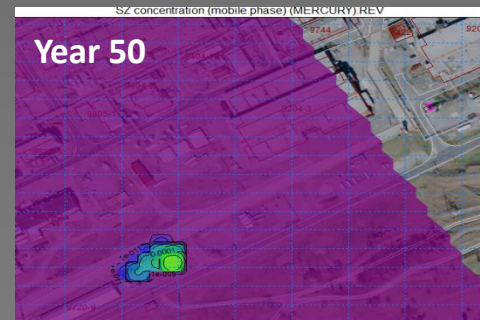
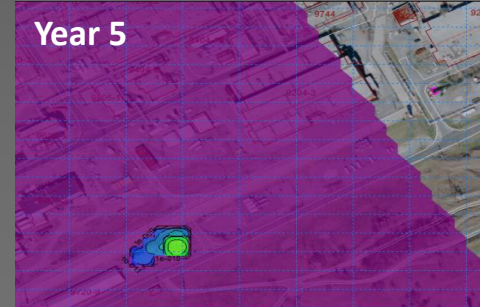
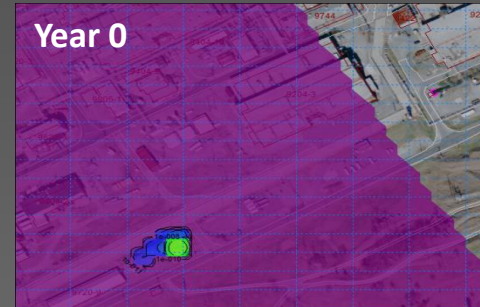
The predicted mercury concentrations in all cases do not exceed the risk-based target groundwater concentration of * 0.036 mg/L (shown by red dashed line in graph) for industrial use scenario.



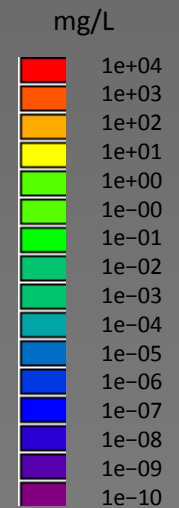
Task 2: TMDL Analysis for EFPC



Non-adsorbing tracer (1 mg/L)
follows groundwater flowpath



Mercury
Mercury has a very limited mobility





Task 2: TMDL Analysis for EFPC

- “ The low solubility of mercury and high retardation factor in the soil near the former Building 81-10 minimize transport of mercury from soil to ground water.
- “ Simulations with a submodel extracted from the watershed model predict that low concentrations of mercury (defined by 10^{-6} mg/L) reached a steady state distribution in ground water 50 meters downgradient of the source within 50 years.
- “ Concentrations in groundwater were below industrial risk levels (0.036 mg/L) by several orders of magnitude. Because the presence of humic acids and other strong ligands can modify the equilibrium concentration of mercury in groundwater and increase transport through groundwater pathways, additional research and modeling is needed to address this uncertainty.
- “ Simulations of mercury contamination in soil didn't create groundwater plumes above industrial risk standards where effective porous media conditions were present and would not influence concentrations in surface water at Station 17.

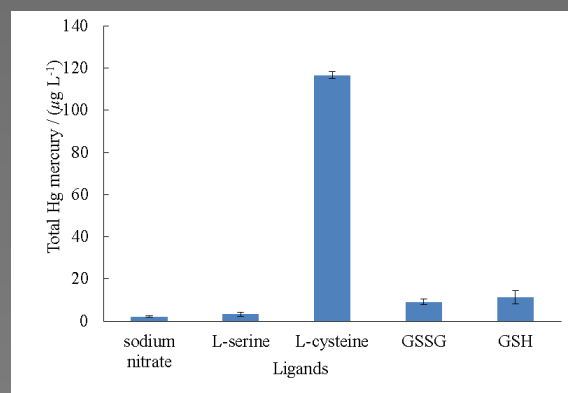


Task 3: Parameterization of Major Transport Processes of Hg Species

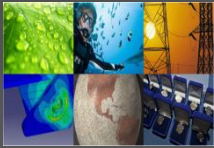
- “ Developed an isotope dilution – flow injection – ICP-MS technique for analysis of Hg species and applied this method to study dissolution of mercury sulfide.
- “ Acquired experimental kinetic and equilibrium data on important parameters related to Hg transport, speciation and transformation in water and sediment.
 - Effect of thiols on mercury sulfide dissolution.



Coupling of a Flow Injection System (FIAS 400) to ICP-MS for analyzing mercury isotopes

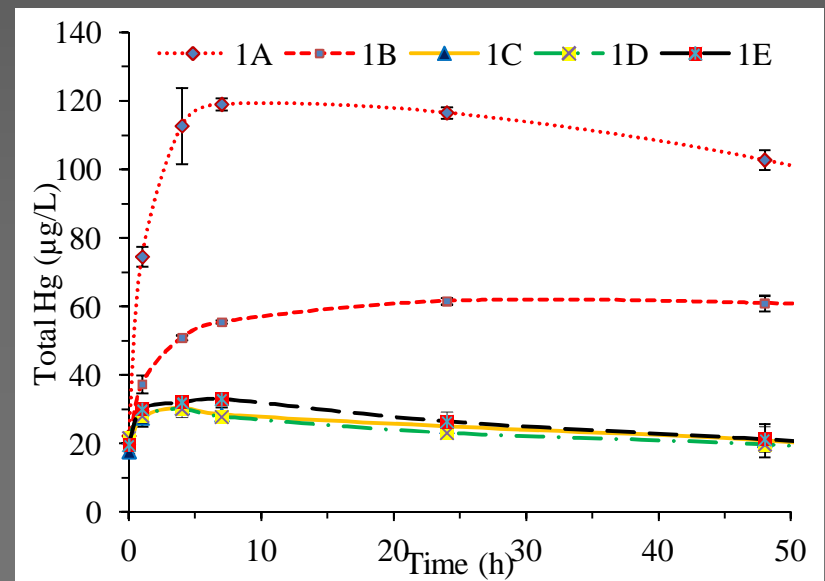


Effect of thiol group on the release of dissolved Hg from cinnabar



Task 3: Parameterization of Major Transport Processes of Hg Species

- “ Used in calibration and sensitivity analysis of numerical model developed for various ORR watersheds (LEFPC, UEFPC, and WOC), by determining acceptable ranges of values certain effective parameters (i.e., partition coefficients and desorption rates) in the sedimentation and water quality modules.
- “ Published several scientific articles in peer-reviewed journals from the experimental results.



Effects of dissolved oxygen on thiol-promoted dissolution of cinnabar. 1A, saturated oxygen; 1B, air; 1C, 1D, 1E, anaerobic condition.



Task 4: Geodatabase Development for Hydrological Modeling Support

- Extended capabilities of EFPC geodatabase developed in FY11 which stores configuration and output data for modeling contaminant flow and transport in EFPC and WOC watersheds at Oak Ridge Reservation (ORR), TN.
- Developed model using ArcGIS ModelBuilder and Python scripting to automate query and export of hydrological modeling data for statistical analysis and the generation of maps, graphs and reports.
- Investigated downloadable free/open source GIS software for online querying of geodatabase so project derived data can be more easily shared with other project stakeholders such as DOE personnel and ORR site contractors.

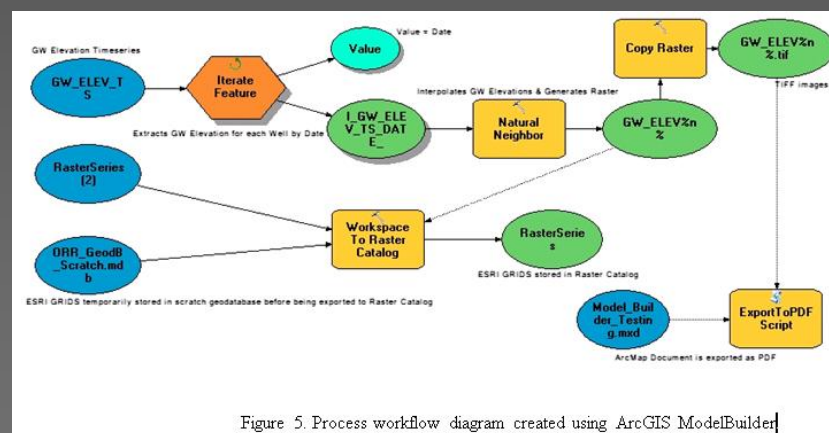


Table 2. Free/Open Source GIS Software Reviewed by ARC-FIU

Software	Version	Operating System	Free/Open Source	Website
ArcReader	10.1	Windows, Mac OS	Free	http://www.esri.com/software/arcgis/arcreader
ArcGIS Explorer Desktop	2500	Windows, Mac OS	Free	http://www.esri.com/software/arcgis/explorer
Quantum GIS	1.8.0	Windows, Mac OS, Linux	Free/Open Source	http://www.qgis.org/
DIVA GIS	7.5	Windows, Mac OS	Free/Open Source	http://www.diva-gis.org/
TatukGIS Viewer	4	Windows	Free	http://www.tatukgis.com/
MapWindow	4.x	Windows	Free/Open Source	http://www.mapwindow.org/
HydroDesktop	1.5	Windows	Free/Open Source	http://hydrodesktop.codeplex.com/
GRASS GIS	6	Windows	Free/Open Source	http://grass.osgeo.org/

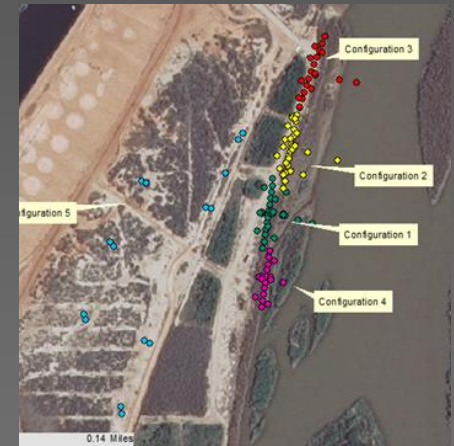


Task 5: Modeling of Groundwater Flow and Transport at the Moab Site

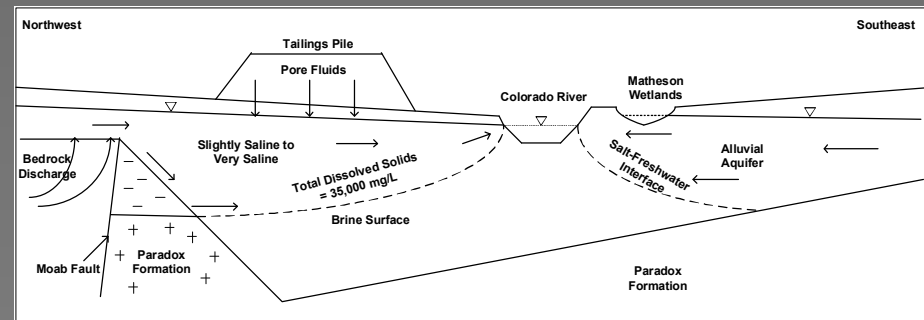
- Reconfiguration of existing Moab model with current spatial and timeseries data. Model calibrated using pumping test data and several years of regular monitoring data to show natural seasonal variations and responses to other stresses.
- Model reasonably matches conceptual mass balance information and replicates expected temporal groundwater flow patterns.
- Difference in measured and modeled groundwater levels likely a function of the assigned Colorado River stage.
- Model predicts approx. 60% water entering groundwater flow system from Moab Wash and bedrock occurs in upper 3 model layers. Result in agreement with conceptual model that hypothesizes recharge and salinity are correlated; the fresher the groundwater, the higher the recharge rate.



Ammonia Concentration



Well configurations



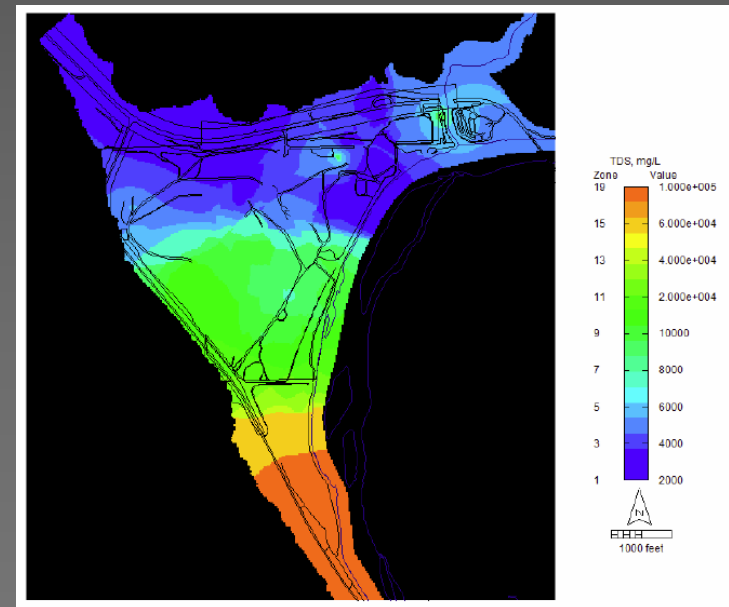
Conceptual model of groundwater system geometry and flow process



Task 5: Modeling of Groundwater Flow and Transport at the Moab Site

- “ Optimization of operation of groundwater extraction well fields, infiltration of treated water, and injection of clean fresh water for DOE UMTRA site in Moab, Utah via:
 - “ Simulation of effectiveness of planned remediation activities for reducing ammonia and uranium concentrations in groundwater that discharges to riparian areas of the Colorado River that contain endangered fish.
 - “ Simulation of effects of discharge of legacy ammonia plume in brine zone beneath site on overlying saline zone.
- “ Simulations will bracket the time to reach cleanup levels.
- “ Models capable of simulating nitrogen and uranium transformations along flow path and density-dependent flow related to brines in groundwater system beneath site.
- “ Simulation of air dispersion of NH_3 from treatment plant air stripper or NH_3 volatilization pond and atomization from spray irrigation on top of pile.

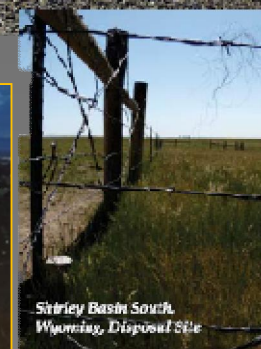
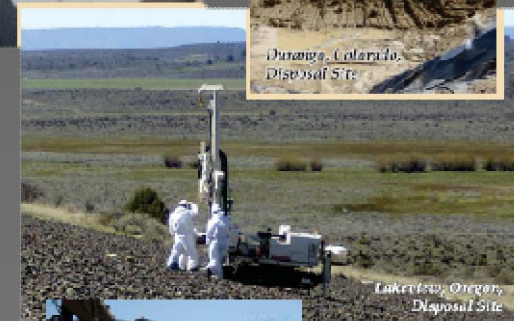
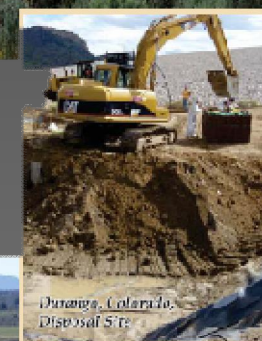
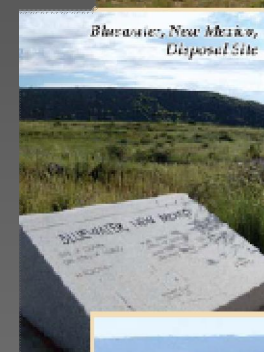
Water Table to 3,945 ft msl TDS concentration

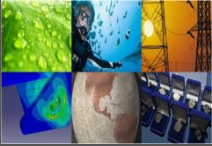




Task 5: Modeling of Groundwater Flow and Transport at the Moab Site

- “ Site Visit to the LM Office at Grand Junction, CO
- “ Met with Dr. April Gil (Environment Team Lead) site managers, and engineering team from Stoller
- “ Attended “UMTRA Regulations and Implementation Workshop” April 9-12, 2013
 - “ GW compliance issues, GW models and the future needs on Geochemical studies of Uranium
 - “ Shiprock , NM; Gunnison, CO; Rifle, CO; Tuba, AZ; Moab, UT; Bluewater, CA; Riverton, WY
 - “ Future collaboration with FIU on the GW and Geochemical modeling





Major Accomplishments - Summary

“ Hydrological Models provide

- . Better understanding of contaminant flow & transport within ORR watersheds.
- . Insight on parameters relevant to ORR environment (e.g. desorption rates of mercury in different media).
- . Critical information via numerical simulations of planned remedial scenarios to assist DOE in making decisions on elements of remediation plans and for meeting TMDL requirements.

“ Laboratory Analyses provide

- . Information on the magnitude and rate of mercury sulfide dissolution under different environmental conditions.

“ Geodatabase

- . Provides centralized spatial and tabular data storage as well as concurrent access and editing capability of observed and simulated model data.



Major Accomplishments - Publications

“ Refereed Journals

- Malek-Mohammadi, S., Tachiev, G., Bostick, K., and Daniel, A. (2013). "Migration of VOC Plume in the Subsurface Domain at the Y-12 National Security Site" Journal of Remediation, Winter 2013.
- Malek-Mohammadi, S., Tachiev, G., Cabrejo, E., and Lawrence, A. (2012). "Simulation of flow and mercury transport in Upper East Fork Poplar Creek, Oak Ridge, Tennessee", Remediation Journal, 22(2), 119–131.
- Li, Y., Yin, Y., Liu, G., Tachiev, G., Roelant, D., Jiang, G., and Cai, Y. (2012). "Estimation of the Major Source and Sink of Methylmercury in the Florida Everglades." Environ. Sci. Technol., 46 (11), 5885–5893.
- Dickson, D., Liu, G., Lib, C., Tachiev, G., Cai, Y. (2012). "Dispersion and Stability of Bare Hematite Nanoparticles: Effect of Dispersion Tools, Nanoparticle Concentration, Humic Acid and Ionic Strength." Science of the Total Environment. 419(1). 170–177.



Major Accomplishments - Publications

“ WM13 Conference Proceedings

- “Long-Term Performance of Uranium Tailings Disposal Cells (13340)”, Georgio Tachiev, Kent Bostic (P2S), Anamary Daniel (P2S), Ken Pill (P2S), Viviana Villamizar, Nantaporn Noosai.
- “Coupling and Testing the Fate and Transport of Heavy Metals and Other Ionic Species in a Groundwater Setting at Oak Ridge, Tennessee (13498)”, Nantaporn Noosai, Hector Fuentes.
- “Recent Approaches to Modeling Transport of Mercury in Surface Water and Groundwater – Case Study in Upper East Fork Poplar Creek, Oak Ridge, TN (13349)”, Georgio Tachiev, Anamary Daniel (P2S), Kent Bostick (P2S).
- “XPSWMM Analysis of the Oak Ridge Stormwater Collection System Up To Outfall 211 (Student Poster)”, Heidi Henderson (DOE Fellow), Georgio Tachiev, Leonel E. Lagos.
- “Improvements and Modifications of an Integrated Flow and Mercury Transport Model for East Fork Poplar Creek, Oak Ridge, Tennessee (Student Poster)”, Lilian Marrero, (DOE Fellow).

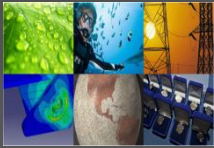
“ Other Conference Proceedings

- “Dissolution of Mercury Sulfide in the Presence of Thiol-containing Substances”, Guangliang Liu, Guidi Yang, Yanbin Li, Sen Chen, Yong Cai, Georgio Tachiev, Leonel Lagos, The 11th International Conference on Mercury as a Global Pollutant (ICMGP).
- “Estimation of the Major Source and Sink of Methylmercury in the Florida Everglades”, Yanbin Li, Yongguang Yin, Guangliang Liu, Georgio Tachiev, David Roelant, Guibin Jiang, Yong Cai, The 9th International Symposium on Persistent Toxic Substances.




Major Accomplishments – Masters Theses/PhD Dissertations

- “ Lilian Marrero, an MS Candidate and DOE Fellow, working with the surface and groundwater model analyzing fate and transport of mercury in the EFPC watershed.
- “ Heidi Henderson, an MS Candidate and DOE Fellow, working with the surface water model analyzing the drainage flows and mercury transport within the ORNL site.
- “ Viviana Villamizar, an MS candidate, developing surface and groundwater model for analysis of tailings at the Moab and Shiprock sites, supporting the work at ORNL.
- “ Nantaporn Noosai, a PhD candidate, developing the thermodynamic database of mercury species and integrating the interactions within a flow and transport model.
- “ Nicole Anderson, a PhD candidate and DOE Fellow, working with the fate and transport model analyzing remediation alternatives for the Moab Site.




Waste Management Symposium 2012



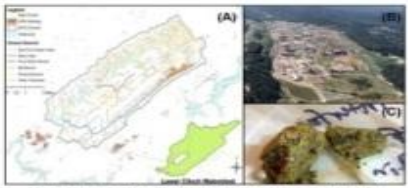
Improvements of an Integrated Flow and Mercury Transport Model in East Fork Poplar Creek Watershed, Oak Ridge, Tennessee

Lilian Marrero (DOE Fellow), Dr. Georgio Tachiev
Applied Research Center, Florida International University, Miami, Florida 33174



Introduction

The environment in the vicinity of Y-12 National Security Complex (Y-12 NSC), Oak Ridge, TN has been contaminated by mercury due to nuclear processing activities during the 1950s. The contamination exists within the soil, shallow groundwater beneath and adjacent to former process buildings, storm sewers, drains, stream sediment, and surface water.



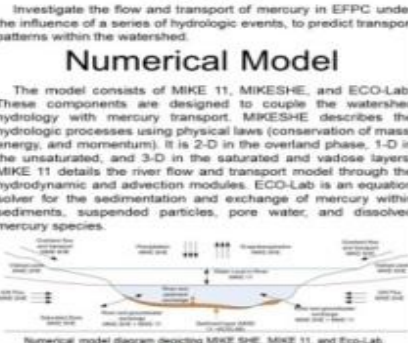
EFPC Watershed (A), Y-12 NSC (B), mercury contaminated soil (C)

Objective

Investigate the flow and transport of mercury in EFPC under the influence of a series of hydrologic events, to predict transport patterns within the watershed.

Numerical Model

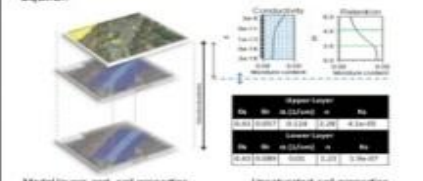
The model consists of MIKE 11, MIKESHE, and ECO-Lab. These components are designed to couple the watershed hydrology with mercury transport. MIKESHE describes the hydrologic processes using physical laws (conservation of mass, energy, and momentum). It is 2-D in the overland phase, 1-D in the unsaturated, and 3-D in the saturated and vadose layers. MIKE 11 details the river flow and transport model through the hydrodynamic and advection modules. ECO-Lab is an equation solver for the sedimentation and exchange of mercury within sediments, suspended particles, pore water, and dissolved mercury species.



Numerical model diagram depicting MIKESHE, MIKE 11, and Eco-Lab.

Methodology

- Processed precipitation, discharges, total mercury, and methylmercury historical data from CREIS database.
- The water quality and sedimentation module was extended to include the entire EFPC, down to station EFK 6.4 and the Bear Creek.
- Update Van Genuchten's hydraulic conductivity and moisture content parameters for the upper and lower portions of the aquifer.



Model layers and soil properties

Unsaturated soil properties

- Water quality, transport related, and sediment related parameters, such as carbon partitioning coefficient, adsorption rates of mercury species to sediment particles and water molecules, re-suspension rate of sediments, settling velocity of suspended particles, and critical current velocity for sediment re-suspension will be estimated from literature.


State Variables	Units	Constraints	Vector
Mercury	0.01 mg/L	Organic carbon adsorption coefficient	0.0001 mg/L
Mercury	0.1 mg/L	Desorption rate to water	1 day ⁻¹
Dissolved mercury in overland zone water	0.1 mg/L	Desorption rate to sediment	0.1 day ⁻¹
Hg sorbed to sediment	10 mg/L	Efficiency of organic carbon in soil	0.1
Suspended matter	10 mg/L	Efficiency of organic carbon in sediment	0.2
Mercury in sediment	10000 mg/L	Thickness of water film	0.1 mm
Mercury in sediment	10000 mg/L	Mercury strength of bonds, organic	50 g/mole
Mercury	10000 mg/L	Details of the sediment	200 mg/m ³ of bulk
Compositional grad/len	2 m	Porosity of sediment	0.85 (pH) / 0.8 (at 24h)
Total water depth	3 m	Settling velocity of SS	0.1 m/sec
Current speed	0.2 m/s		

ECOLAB state variables, constants, and forcing


- Simulations executed for a range of input parameters to correlate stochastic hydrologic events with mercury distribution patterns.

Results

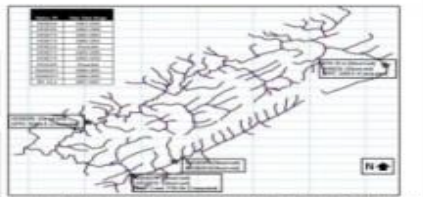
Successfully executed a 15 year simulation (1991 – 2005) for water movement and water quality, including Eco-Lab to assess the impact of the hydraulic parameters and determine the best fit with observed data.



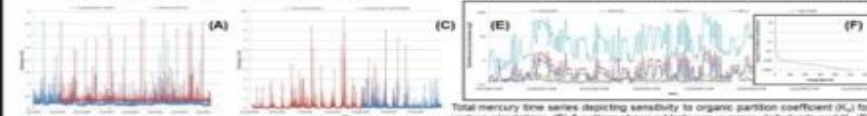
Computed discharge time-series for Bear Creek 7700.06




Computed total mercury time-series for Bear Creek 7700.06




Model network depicting tributaries, computational nodes, and field stations.




Total mercury time series depicting sensitivity to organic partition coefficient (K_d) for various simulations (E) & pattern observed between average daily loads and K_d (F)




Comparison of computed discharges (A) & probability exceedance curves (B) at EFPC 3209.9 & field station EFK 23.4



Comparison of computed discharges (C) & probability exceedance curves (D) at Bear Creek 7700.06 and field station 03536270



Load duration curves downstream EFPC



Load duration curves downstream Bear Creek

Conclusions

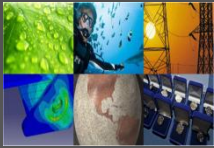
- Mercury attenuates downstream of EFPC
- Sediment-mercury interactions significantly affect Hg transport.
- High flow conditions re-suspend mercury particulates increasing concentration in the creek.
- Total mercury concentrations appear sensitive to the organic partition coefficient introduced via the water quality module.

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- FIU, 2002. Integrated Surface and Subsurface Mercury Transport Model of a US National Security Complex, Oak Ridge, Tennessee.
- Marrero, L. and Tachiev, G. An Integrated Flow and Transport Model to Study the Impact of Mercury Remediation Strategies for East Fork Poplar Creek Watershed, Oak Ridge, Tennessee, Florida International University, Environmental Eng. Dept., Master Thesis.

Acknowledgements: Dr. Georgio Tachiev, Dr. Siamak Malek-Mohammadi, Angelique Lawrence, Dr. Leonel Lagos, DOE/FIU Science & Technology Workforce Development Initiative

Presented poster "Improvements of an Integrated Flow and Mercury Transport Model in East Fork Poplar Creek Watershed, Oak Ridge, Tennessee."



Waste Management Symposium 2013

BRADLEY UNIVERSITY

Pro2Serve
Professional Project Services, Inc.

Groundwater Transport of Organic Compounds, Y-12, Oak Ridge, TN
Samsak Malik-Muhammad¹, Georgio Tachian², David Rowland³, Kent Bostick⁴, Anamary Caniel⁵
¹Civil Engineering and Construction Department, Bradley University, Peoria, IL 61619
²Applied Research Center, Florida International University, Miami, FL 33174
³Pro2Serve Professional Project Services, Inc., Oak Ridge, TN 37830

FIU Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

Introduction

During the operation of U.S. National Security Complex (Y-12), the surrounding environment has been contaminated with considerable amounts of volatile organic compounds (VOCs) arising at other manufacturing units on heavy metals, radionuclides, and solvents. It is estimated that much of the VOCs are adsorbed in soil, sediments, and groundwater at the vicinity of Y-12. The model simulates the adsorbed hydrology with the VOC transport.

Y12

Figure 1: Aerial view of Y-12

Numerical Model

An integrated aquifer and groundwater flow and transport model was developed for the Y-12 site, using MODFLOW, to simulate the flow and transport of VOCs including PCE, 1,1-DCE, and 1,1,1-TCE and to estimate the soil and groundwater at the vicinity of Y-12. The model simulates the adsorbed hydrology with the VOC transport.

Parameter	Value	Unit
Porosity	0.35	-
Hydraulic conductivity	1.0E-01	m/d
Dispersion coefficient	1.0E+01	m
Retention factor	1.0	-
Decay constant	0.0	1/d

Figure 2: Numerical model diagram

Results

The groundwater flow is simulated using the advective collection of water table results from the MODFLOW. Groundwater depth is higher at the ridge on the north and U-shaped ridge on the south and lower in the valley. The groundwater depth distribution varies, and the flow direction varies the direction of unconfined water in response, especially in dry seasons.

Figure 3: Groundwater depth distribution

Figure 4: Cross-section plot of groundwater depth

Figure 5: Hydraulic conductivity distribution

Figure 6: Cross-section plot of groundwater velocity

Figure 7: Cross-section plot of groundwater concentration

Figure 8: Cross-section plot of groundwater concentration

Conclusions

1. PCE, 1,1-DCE, and 1,1,1-TCE are not detected in soil with exception to soil in unconfined groundwater table and the table. Maximum values are listed in table below.

Depth	Location	PCE (mg/kg)	1,1-DCE (mg/kg)	1,1,1-TCE (mg/kg)
0-10 cm	Area 1	1.0E+01	1.0E+01	1.0E+01
10-20 cm	Area 2	1.0E+01	1.0E+01	1.0E+01
20-30 cm	Area 3	1.0E+01	1.0E+01	1.0E+01
30-40 cm	Area 4	1.0E+01	1.0E+01	1.0E+01
40-50 cm	Area 5	1.0E+01	1.0E+01	1.0E+01
50-60 cm	Area 6	1.0E+01	1.0E+01	1.0E+01
60-70 cm	Area 7	1.0E+01	1.0E+01	1.0E+01
70-80 cm	Area 8	1.0E+01	1.0E+01	1.0E+01
80-90 cm	Area 9	1.0E+01	1.0E+01	1.0E+01
90-100 cm	Area 10	1.0E+01	1.0E+01	1.0E+01

2. Results of the MODFLOW model are compared with the results of MODFLOW-GWT model. Results derived in the MODFLOW model are greater in mass and mobility, the results derived here are considered to be in good line with the predicted concentrations.

Parameter	Value	Unit
Porosity	0.35	-
Hydraulic conductivity	1.0E-01	m/d
Dispersion coefficient	1.0E+01	m
Retention factor	1.0	-
Decay constant	0.0	1/d

3. VOC concentrations in soil and groundwater table were measured groundwater table and found table within approximately 20 feet.

Path Forward

1. Comparing the model with the latest field measurements of VOC concentrations in groundwater and soil, identify the direction of VOC movement.

2. Investigating the results transport of VOCs which contains the location among VOCs, radionuclides, and solvents present of the groundwater and soil at the site.

References



1. U.S. DOE, 1984, Remedial Investigation of the Upper East Fork Poplar Creek (Characterization Area) at the Y-12 Plant, Oak Ridge, Tennessee, SAND/DOE-1984-111, Environmental Sciences Systems, Springfield, Virginia.

2. USDOE, 2002, The Upper East Fork Poplar Creek (Characterization Area), Sand/DOE-2002-111, Environmental Sciences Systems, Springfield, Virginia.

Awarded Best Professional Poster at WM 2013 for poster entitled "Groundwater Transport of Organic Compounds, Y-12, Oak Ridge, TN" which was presented during WM 2012.




Waste Management Symposium 2013

Long-term Performance of Uranium Tailings Disposal Cells.

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*Applied Research Center, Florida International University, Miami, FL 33174
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Introduction

Recently, there has been interest in the performance and evolution of Uranium Mill Tailings Remedial Action (UMTRA) Project disposal cell covers. The Project involved remediation of 24 uranium tailings sites between 1950s and 1990s, most of which are in the western United States. Some compliance issues may be related to transient drainage of moisture in the tailings and legacy sources other than the remediated tailings. Prior to recognition of the proposed EPA groundwater protection standards by the UMTRA Project, beginning in 1955, UMTRA Project disposal cells consisted of uranium tailings and other contaminated materials covered by a one-to two-meter thick clay radon barrier, overlain by 1.5 centimeters (cm) of filter sand and 30 cm of erosion protection riprap (Figure 1). The design goal for the radon barrier in the cover was to obtain a saturated hydraulic conductivity on the order of 10⁻⁷ centimeter per second (cm/s). The filter layer consists of a sand with a hydraulic conductivity of 0.001 to 1.0 cm/s, and protects the radon barrier from erosion, facilitates drainage off the radon barrier, and allows for evaporation of residual moisture.

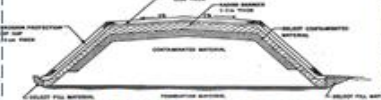


Figure 1. UMTRA Disposal Cell Design Prior to 1955

Tailings that were remediated in place at this time may have had a perched organic surface with in the tailings and tailings that were relocated from flood sites were compacted with optimum and heavily watered for dust control. These practices may have contributed to high percentages of saturation in the tailings. Seepage rates through the radon barrier at a rock-covered disposal cell are equal to the product of the hydraulic conductivity (a function of the moisture content) and the hydraulic gradient. For moisture contents that are vertically uniform, the hydraulic gradient is unity. However, using the saturated hydraulic conductivity of 1 X 10⁻⁷ cm/s in the radon barrier for the purpose of calculating seepage rates is highly conservative and in some cases produces demonstrating compliance with the ground water standard. If the radon barrier is unsaturated, potential hydraulic conductivities of the radon barrier and long-term seepage rates from the facility may be several orders of magnitude lower.

Midway through the project in 1955, the DOE began to comply with U.S. Environmental Protection Agency (EPA) groundwater standards applicable to the UMTRA Project (40 CFR 192). They established concentration limits for hazardous constituents that cannot be exceeded at the down gradient limits of the disposal facility (the point of compliance, or POC) (DOE 1999). Goals were changed to eliminate these three radon progenies in the radon barrier and allowed for vegetation on the top surface. Relocated tailings and cell covers were compacted dry of optimum, and watering for dust control was minimized. Presently, covers are maintained to prevent vegetation, however, as a vegetated cover is a probable plant succession and state questions have arisen whether the covers will perform as vegetation encroaches and whether seepage in cover layers occurs and effects disposal cell performance. If cover is shaped to shed surface water runoff,

Field Observations

Core samples from cores of early UMTRA covers at the Shirock, Ohio, UT and Sunbelt, PA sites indicate that average percent saturations were 54, 52, and 62% respectively three years after placement of the covers. Neutron moisture meter monitoring indicates relatively uniform moisture content below the top 0.3 m of the radon barrier (Figure 2). Recently in 2011 higher percent saturations have been reported at some locations in the radon barrier at Shirock. Daily precipitation and evaporation for the period 2000 to 2011 are shown in Figures 3 and 4, respectively.

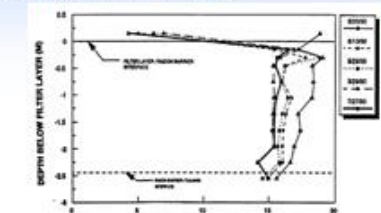


Figure 2. Neutron Meter Moisture Contents with Depth in the Radon Barrier in the Shirock, UMTRA Disposal Cell

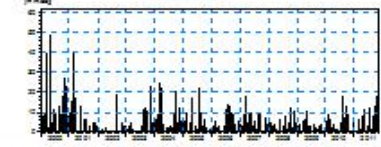


Figure 3. Daily Precipitation at the Shirock UMTRA Site

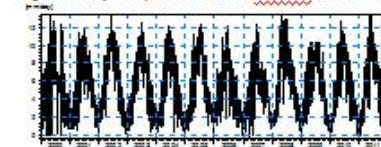


Figure 4. Daily Evapotranspiration at the Shirock UMTRA Site

Modeling Approach

A unique modeling approach allowed simulation with daily climatic conditions to determine changes in moisture and moisture flux from the disposal cell. The numerical model is based on the MIKE SHE/MIKE 11 modeling system from DHI Water & Environment [6]. The model requires data in standard GIS format. Spatial data for Shirock was obtained from USGS National Map Viewer. The modeling approach is superior to previous modeling because it is 3-dimensional and includes the full stratigraphic column from the cover down to and including groundwater in the aquifer on the escarpment. This allows for integrated POC compliance modeling within one model. In addition, the approach allows for modeling of daily climatic parameters and can be used to determine the effect, if any, of extreme events within the period of record rather than simulation of average monthly conditions. The model domain consists of the tailings disposal cell and a surrounding region of shallow groundwater on the escarpment as shown in Figure 5.




Figure 5. Model Domain

The top boundary of the model used measured daily rainfall from the Western Regional Climate Center (10) from 2000 to 2011 (Figure 4) and calculated evapotranspiration as a variable prescribed upper boundary (Figure 5).

Tailings were assumed to be initially saturated and the radon barrier had an initial condition of 54.0 percent saturation. The unsaturated hydraulic properties were described using the pore size distribution model of Mualem (11) for the hydraulic conductivity in combination with a water retention function introduced by Van Genuchten. Simulations were conducted using a ten-year period of daily time series (precipitation and evapotranspiration). Ten years was a suitable time period as moisture contents became relatively stable with depth in the cover within a simulation period of two years. The objective of the simulations was to determine the range of variability of infiltration fluxes and moisture contents within the model layers. Figure 6 shows the rate of infiltration at the surface of

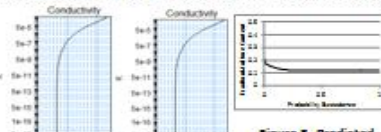


Figure 6. Predicted Probability of Moisture Content at the Top of the Radon Barrier

Figure 7. Unsaturated Conductivity Function for Sand Layer and Radon Barrier. A graph showing unsaturated conductivity function for sand layer and radon barrier.

Results and Conclusions

Although there is a direct correlation between rainfall events and infiltration rates, the water balance (Figure 8) demonstrates the cumulative evapotranspiration from the cover. This implies there is no water reaching the disposal surface in the tailings, at least there is no downward moisture flux. Furthermore, salinization and encroaching vegetation on the rock layer does not significantly impact the cover performance.




Figure 8. Predicted Cumulative Water Balance

Figure 9 shows the depth of the unsaturated zone from the surface. At the location of the disposal cell the depth of unsaturated zone (saturation less than 1.00 percent) extends to more than 20 ft below the top of the cover. This means that in 10 years, transient drainage from the tailings has lowered the moisture content to 10 ft.

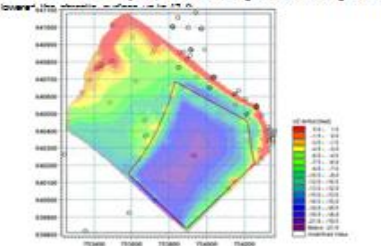


Figure 9. Predicted depth of saturation

The model confirmed the following trends:

- water balance indicates no deep infiltration through the cover;
- a low moisture content in sand (0.2) above the radon barrier yields a low conductivity of 10⁻¹⁰ m/s;
- vegetation increases the rate of evapotranspiration

Successionary evolution of rock covers will not hinder their performance in any manner.

Contact Information: Kent Bostick, kbo@fiu.edu, 305 559-1283
Georgio Tachiev, tachiev@fiu.edu, 305-313-0733

Presented poster "Long-term Performance of Uranium Tailings Disposal Cells"



Internships



DOE Fellow Lilian Marrero with mentor Dr. Jennifer Knoepfle at Sullivan International Group, Inc., Chicago, IL



DOE Fellow, Heidi Henderson with mentor Dr. Eric Pierce at Oak Ridge National Laboratory

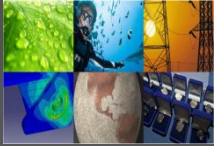


DOE Fellow, Alex Henao at Moab UMTRA Project site, UT



Path forward and future work

- “ The proposed retardation factor, although conservative, can be influenced by colloidal transport or complexation with ligands in the groundwater system.
- “ In addition, the solubility of the mercury (60ppb) was used as a limiting factor for transport of aqueous mercury from liquid elemental mercury sources, however this is valid for only a pure system. In a real system this limit is a function of organic content of groundwater and presence of ligands which have high affinity to mercury.
- “ The modeling investigated only transport through shallow groundwater pathways under porous media conditions for sources in soil. It should be recognized that site characterization has indicated that the area under the UEFPC is underlain by the Maynardville Limestone that contains karst conduits. Mercury sources within the limestone and transport to UEFPC may also contribute to total mercury flux at Station 17.



Future Work (FY13)

” Task 1: EFPC Model Update, Calibration, Uncertainty Analysis

- Use updated EFPC model to simulate selected main thermodynamic equilibria and reactions. Will support PhD student.

” Task 2: Simulation of NPDES & TMDL Regulated Discharges from Non-Point Sources for EFPC & Y-12 NSC

- Develop surface flow model for Y-12 NSC, similar to ORNL model, to determine discharges from stormwater drainage system and outfalls along EFPC. Simulations will provide numerical analysis of contaminant flow and transport within EFPC watershed and will determine impact of model parameters on NPDES and TMDL regulations. Will support 2 MS students.

” Task 3: Environmental Remediation Optimization: Cost Savings, Footprint Reductions, and Sustainability Benchmarked on DOE Sites

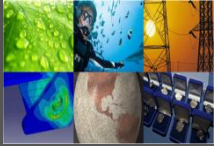
- Use of SITEWISE™ sustainability software will be benchmarked at one or more EM field sites with pilot-scale studies where cost benefit can be demonstrated. FIU will work with EM HQ and interested field sites to obtain field data for pilot-scale sustainability evaluations using SITEWISE™.

” Task 4: Geodatabase Development for Hydrological Modeling Support

- Update geodatabase (gdb) with recent ORR site/environmental data. Develop library of customized Python scripts to enhance gdb querying capabilities and couple with existing libraries used for mathematics, science, and engineering (e.g. NumPy and SciPy) to perform statistical analyses. Provide training to students on updating and querying gdb. Use existing gdb structure to create similar databases to support modeling work conducted at Moab and DOE Idaho Sites.

” Task 5: Student Support for Modeling of Groundwater Flow and Transport at the Moab Site, Utah

- Determine effect of discharge of legacy ammonia plume from brine zone during operation of extraction wells and injection system, and after shut off using daily simulation timesteps. Model will be used to predict capture zones for different operating scenarios, mass removal, and time to complete remediation. PhD student will work with transport model to perform numerical simulations of remedial scenarios and develop PhD dissertation.



Project Clients & Collaborators



Moab, Utah, UMTRA Project



OAK RIDGE NATIONAL LABORATORY

Managed by UT-Battelle for the Department of Energy