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
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Staff and Students

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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 physciochemical 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.
- 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.
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 (Kd) for Kd=0.025 (red), Kd=0.05 (blue), Kd=0.5 (green), Kd=5 (purple), and Kd=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.
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](image1)

- Tested two hypotheses of metal transport in the Ca-Mg-HCO$_3$ 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](image2)

![Transport of Hg in groundwater at Y-12 plant with role of ion exchange and sorption on Fe(OH)$_3$](image3)
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 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 referenced
- Flow data 100,000 records
- Mercury concentration data in surface water

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OREIS Database (Query: Oct 2010)
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 contributed to the flux of mercury at Station 17. Because colloidally adsorbed 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

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 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 groundwater.

- 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 groundwater 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.

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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.

Conceptual model of groundwater system geometry and flow process

Ammonia Concentration
Well configurations
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


Major Accomplishments - Publications

**WM13 Conference Proceedings**


- “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.


- “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**


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