YEAR END TECHNICAL REPORT

May18, 2012 to August 17, 2013

Remediation and Treatment Technology Development and Support

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Addendum:

This document represents one (1) of five (5) reports that comprise the Year End Reports for the period of May 18, 2012 to July 17, 2013 prepared by the Applied Research Center at Florida International University for the U.S. Department of Energy Office of Environmental Management (DOE-EM) under Cooperative Agreement No. DE-EM0000598.

The planned period of performance for FIU Year 3 under the Cooperative Agreement was May 18, 2012 to May 17, 2013. However, two no-cost extensions have been executed by DOE-EM. The first no-cost extension was received from DOE on 05/17/13 to extend the end of the period of performance for a period of two months (until 07/17/13). Another two months no-cost extension was received from DOE on 07/10/13 to extend the end of the period of performance to 9/16/13. The activities described in this report are for the FIU Year 3 period of performance from May 18, 2012 to August 17, 2013.

The complete set of FIU's Year End Reports for this reporting period includes the following documents:

1. Chemical Process Alternatives for Radioactive Waste
   Document number: FIU-ARC-2013-800000393-04b-213
2. Rapid Deployment of Engineered Solutions for Environmental Problems at Hanford
   Document number: FIU-ARC-2013-800000438-04b-217
3. Remediation and Treatment Technology Development and Support
   Document number: FIU-ARC-2013-800000439-04b-219
4. Waste and D&D Engineering and Technology Development
   Document number: FIU-ARC-2013-800000440-04b-216
5. DOE-FIU Science & Technology Workforce Development Initiative
   Document number: FIU-ARC-2013-800000394-04b-072

Each document will be submitted to OSTI separately under the respective project title and document number as shown above.

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PROJECT 3 OVERVIEW

Approximately 75 to 150 metric tons of elemental mercury (used in a lithium-isotope separation process for production of nuclear fusion weapons), were released into East Fork Poplar Creek (EFPC) watershed from the Y-12 National Security Complex (Y-12 NSC) in eastern Tennessee, USA. Under typical environmental conditions, elemental mercury is oxidized to mercuric ion which has a greater solubility and mobility in groundwater and surface water. The increased mobility of the mercuric ion results in elevated concentrations of total mercury in soil, surface water and groundwater. The mercuric ion has high affinity to many organic ligands and in the water column the majority of the mercuric ions are bound to suspended and colloidal particles. Storm events increase the turbulence and velocity of river flow and may result in additional mobilization and transport of mercury downstream in the EFPC.

In order to analyze the mercury cycle in the environment and to provide forecasting capabilities for the fate and transport of contamination within the watershed, an integrated surface and subsurface flow and transport model for the Y-12 NSC was developed. The model couples the hydrology of the watershed with mercury transport and provides a tool for analysis of changes of mercury load as function of changes in hydrology, including remediation scenarios which modify the hydrological cycle. The model couples the overland and subsurface flow module with the river flow and transport module. The model includes the main components of the hydrological cycle: groundwater flow (3D saturated and unsaturated), 2D overland flow, 1D flow in rivers, precipitation, and evapotranspiration. Furthermore, the model includes 57 outfalls along Upper East Fork Poplar Creek (UEFPC) which have been listed in the National Pollutant Discharge Elimination System (NPDES) permit from 2005. A sedimentation module was included to simulate the interactions between sediment particles, water and mercury species within the EFPC.

The numerical model was calibrated for the period of 1996-2009 using recorded stream flow and mercury concentrations measured in groundwater, surface water and soil. The model was subsequently applied to evaluate the effect of nine remediation strategies/scenarios in the UEFPC region on reducing the mercury concentrations. For each remediation scenario, flow duration curves and mercury load duration curves were compared at Station 17 for the computed and recorded data. The remediation efficiency was determined by comparing the percent daily reduction of mercury discharges downstream of Station 17. The results of numerical simulations showed that exchange of mercury species between sediment, pore water, aqueous media and suspended solids significantly affects the mercury load detected at Station 17.

A series of laboratory studies were conducted to analyze the effect of various environmental factors (pH, pE) on methylation and demethylation processes in the water column. Experimental work was used to obtain critical mercury exchange parameters between pore water, colloidal and suspended particles, and streambed sediment, which were applied in the numerical model to study the effect of sediment transport on mercury mobilization.

For year 2010-2011, the model, which was developed for the Y-12 NSC, was extended to include the EFPC watershed and the creek between Y-12 NSC and Station EFK 6.4. The research focused on conducting additional simulations using the EFPC watershed model which extend the studies for Y-12 NSC. In addition, flow and transport studies were conducted for the Bear Creek watershed (a sub-watershed of the larger EFPC watershed). A geodatabase was also developed as a strategy for supporting hydrological model data input by creating a centralized data storage system to store model parameters instead of a collection of data layers, which provides a more stable foundation for building GIS-based water resources applications.

For FY 2012, FIU proposed a scope which relied on previously developed models of EFPC to provide simulation of fate and transport of contaminants and remedial activities. Stochastic analysis was performed on measured hydrological and transport data including flow and pollutant concentrations at each outfall. A detailed mass balance was developed for the site for contaminants of concern, including inorganic (Hg) and organic contaminants. The work provides insight on the contribution of each outfall to the load at Station 17. The laboratory work included additional studies to determine experimental parameters related to cinnabar dissolution and contribution for mercury distribution between various phases (aqueous and soil) for different environmental factors including pH, dissolved oxygen, dissolved organic matter, organic and inorganic content of soils and pore water, on mercury fate and transport within the creek and for overland flow. The work will provide a better understanding of the mercury dynamics within the Oak Ridge Reservation watersheds (EFPC, Y-12 NSC, Bear Creek, White Oak Creek) for variable environmental conditions and for specified remediation alternatives. Student support was also provided for numerical modeling of subsurface flow and transport at Moab site.

TECHNICAL PROGRESS SUMMARY FOR FY12

During FY2008-2012, FIU developed integrated flow and transport models of East Fork Poplar Creek (EFPC), Upper EFPC (Y-12 NSC) and White Oak Creek (WOC) watersheds at the Oak Ridge (OR) site, and conducted numerical modeling and reviews of monitoring data available from OREIS and related to mercury contamination and remediation within these watersheds. A surface water flow and transport model was developed to provide information about the quantities, frequencies and concentrations resulting from stormwater drainage and discharging through a number of outfalls in the upper section of the EFPC and WOC. The model showed excellent accuracy for the measured flow events in the drainage system. In addition, experimental studies provided experimental kinetic and equilibrium data about important parameters related to mercury transport, speciation and methylation/demethylation kinetics within the watershed. A variable density model, which was developed by site contractors for the Moab site, was used to provide simulations of several scenarios related to creating a hydraulic barrier between the mine tailings stored at the site and ecologically sensitive areas of the Colorado River. A geodatabase was developed for storing experimental and computed data for the OR and Moab sites. The following outlines project-wide and individual task accomplishments for FY2012.

- A draft Project Technical Plan for FY2012 (FIU Year 3) was prepared and sent to DOE on June 25, 2012. (See P3 APPENDIX I: FY12 PROJECT TECHNICAL PLAN)
- Project progress overviews and accomplishments were presented to DOE HQ and DOE ORO (August 2012, April 2013 and June 2013). (See P3 APPENDIX II: PROJECT OVERVIEW PRESENTATIONS)
- Progress Reports were submitted as milestones throughout the fiscal year and include:
    - A report presenting the XPSWMM model preliminary configuration parameters (September 2012) and a summary report of preliminary simulation results (November 2012) both related to Subtask 1.3a: Surface Water Flow and Contaminant Transport Model of ORNL 4500 Area. (See P3 APPENDIX III: PROGRESS REPORT - XPSWMM MODEL PRELIMINARY CONFIGURATION PARAMETERS and P3 APPENDIX IV: PROGRESS REPORT - XPSWMM MODEL PRELIMINARY RESULTS SUMMARY)
    - A summary report of results derived from preliminary laboratory experiments (January 2013) conducted under Task 3: Parameterization of Major Transport Processes of Mercury Species. (See P3 APPENDIX V: PROGRESS REPORT - PRELIMINARY RESULTS SUMMARY OF LABORATORY EXPERIMENTS)
    - A report presenting sample Python scripts and Model Builder process workflow diagrams (February 2013) related to Task 4: Geodatabase Development for Hydrological Modeling Support. (See P3 APPENDIX VI: PROGRESS REPORT - SAMPLE PYTHON SCRIPTS AND MODEL BUILDER PROCESS WORKFLOW DIAGRAMS)
    - A summary of preliminary simulation results for the Moab Model (October 2012) conducted under Task 5: Student Support for Modeling of Groundwater Flow and

Transport at Moab Site, Utah. (See P3 APPENDIX VII: PROGRESS REPORT - PRELIMINARY RESULTS SUMMARY FOR THE MOAB MODEL)

- Four (4) peer reviewed journal articles were published based on research conducted for this project (See P3 APPENDIX VIII: PUBLICATIONS):
  - 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*, 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." *Environmental. Science & Technology*, 46(11), 5885–5893.
  - Dickson, D., Liu, G., Lib, C., Tachiev, G., and 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.
  - Malek-Mohammadi, S., and Tachiev, G. (Winter 2013). "Migration of VOC Plume in the Subsurface Domain at the Y-12 National Security Site." *Remediation*, 23(1), 139-153.
- Research results were also presented at various conference proceedings throughout the year (See P3 APPENDIX IX: CONFERENCE PROCEEDINGS) including:
  - <u>The 9th International Symposium on Persistent Toxic Substances, October 2012.</u>
    - "Hydrologic and Kinetic Parameters Impacting the Total Mercury Transport within the EFPC Watershed of Oak Ridge Reservation", Lilian Marrero, Georgio Tachiev, Nantaporn Noosai.
    - "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,
  - <u>The Waste Management Conference 2013 (WM13), February 2013.</u>
    - "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).
  - <u>The 11th International Conference on Mercury as a Global Pollutant (ICMGP).</u>

    - "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,

- Technical Reports for all the tasks related to this project have also been submitted to DOE as follows:
  - Tasks 1 & 2 were based on the students Lilian Marrero, Heidi Henderson and Nantaporn Noosai's thesis work and have been combined into a single technical report with various subsections. (See P3 APPENDIX X: T1T2-001: TASKS 1 & 2 TECHNICAL REPORT).
  - The Task 3 technical report is entitled "Parameterization of Major Transport Processes of Mercury Species". (See P3 APPENDIX XI: T3-001: TASK 3 TECHNICAL REPORT)
  - The Task 4 technical report is entitled "Geodatabase Development for Hydrological Modeling Support". (See P3 APPENDIX XII: T4-001: TASK 4 TECHNICAL REPORT)
  - The Task 5 technical report is entitled "Modeling of Groundwater and Flow and Transport at the Moab Site in Utah". (See P3 APPENDIX XIII: T5-001: TASK 5 TECHNICAL REPORT)
- Three Master's theses and a PhD dissertation are being pursued based on this project work, specifically Task 3.1 "EFPC Model Update, Calibration, and Uncertainty Analysis" and Task 3.5 "Student Support for Modeling of Groundwater Flow and Transport at the Moab Site, Utah".
  - 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.
- This project overall has provided training for 5 DOE Fellows and provided 5 student internships.

TASK 1: EFPC MODEL UPDATE, CALIBRATION AND UNCERTAINTY ANALYSIS

INTRODUCTION

This research is a continuation of efforts to correlate the hydrology of the East Fork Poplar Creek (EFPC) and Bear Creek (BC) with the long-term distribution of mercury within the overland, subsurface, river, and vadose zone sub-domains. The main objectives of this task were to extend the existing EFPC model by adding sedimentation and reactive transport modules, and to use the model to perform numerical simulations that are relevant for the NPDES and TMDL regulations. The simulations provide a better understanding of the flow and transport within the watershed on a regional scale. Simulations were conducted using historic observations of rainfall, evapotranspiration, and contaminant distribution within the watershed to determine transport patterns within the domain. The application seeks to demonstrate the capability of the enhanced model to support efforts to understand and manage mercury contamination and remediation. During FY11, the focus was on extending the sedimentation module to include the entire EFPC and Bear Creek. This research has also provided stochastic modeling of the system and has included an analysis of the spatial and temporal patterns as a result of the stochastic variations of selected properties of the sub domain. In FY12 FIU continued using the numerical model of EFPC to determine the impact of remediation alternatives on the complete hydrologic cycle, the transport overland and in surface water and rivers, sediment transport and reactions, and mercury exchange with sediments. This research was coordinated with the site and ORNL personnel.

In addition, a model was developed which replicates the storm water management system of ORNL's Outfall 211 and its contributing drainage areas using XPSWMM modeling software in order to assess flood risks. In order to understand the transport of contaminants, it is critical to understand the flow of water within the area of interest. Thus, a conceptual stormwater management model was developed for flood risk analysis of Outfall 211 as well as other contributing drainage sources from the adjacent buildings, such as cooling water and condensate from various AC units and discharge from the Creep Laboratory (Building 4500S). Model development was conducted using an approach that can be extended to the Y-12 National Security Complex. The ORNL domain being modeled is at a smaller scale than the Y-12 area and will act as a test bed for Y-12, as both facilities were built using similar construction and drainage methods.

The following summarizes the results and conclusions derived from research conducted under this task throughout the FY12 period of performance. Further details are reported in the attached technical report under P3 APPENDIX X: T1T2-001: TASKS 1 & 2 TECHNICAL REPORT.

SUBTASK 1.1 & 1.2: RESULTS AND DISCUSSION

- The EFPC model which was previously developed has been extended and improved throughout the course of this study as reflected by Figure 1. The model has been extended to include observation stations not previously considered within the MIKE SHE module. This was performed upon evaluating the most recent publicly available historical data for the site.
- Internal numerical parameters within the simulation specifications were evaluated and updated to decrease the computational time within the model's pre-processing, water movement, and water quality computational phases. In addition, data was reformatted to increase pre-processing speed. For example, vegetation data input format was changed from shape to gridded codes.
- The MIKE 11 component of the model also underwent various transformations. The AD module was modified to include ECO Lab, the watershed river network was extended significantly when compared to the baseline EFPC Watershed model, and cross-sections were added to reduce flooding at points of high numerical instabilities.
- Existing river cross-sections were also examined and altered to ensure consistency in bed level elevations at the branch junctions and thus reduce numerical instabilities. Furthermore, the newly incorporated
- ECO Lab template was adjusted to include state variables, forcing, values, and constants previously defined for the localized Y-12 model. A more detailed overview of the changes implemented to the baseline model is shown in the Year End Technical Report for this task.

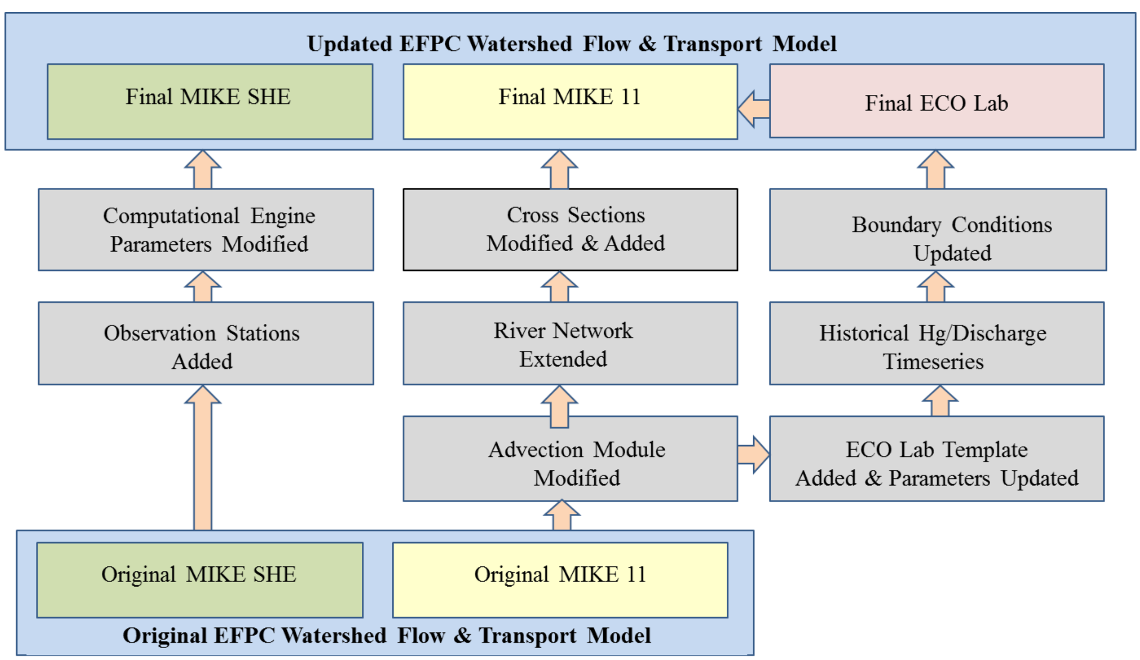

Figure 1. Overview of EFPC model update.

- A thesis has been drafted which relates to the work being conducted under this Project 3 Task 1 as well as Task 2.

SUBTASK 1.1 & 1.2: CONCLUSIONS

Modeling software MIKE SHE, MIKE11, and ECO Lab were combined in a comprehensive package that models the flow and transport of mercury in exchange with sediment and sediment pore water. The application includes an analysis of spatial and temporal patterns stimulated by variations of selected properties of the sub domain. The impact of sedimentation on the fate of mercury was assessed through a series of simulations and using the sedimentation layer module (ECO Lab); this module addresses the dissolved mercury in the water, the adsorbed mercury concentration on suspended matter, the dissolved mercury in sediment pore water, and the adsorbed mercury in the sediment.

In the application of the model to the EFPC watershed, previous modeling efforts, which originally included only the upper portions of EFPC, were extended to include the entire EFPC, down to station EFK 6.4 and the BC. The model is capable of simulating the entire hydrological cycle. Water quality, transport, and sediment related parameters were updated based on DOE experimental reports and journal publications to include observed data of flow, stage, and mercury concentrations in soil, surface water, groundwater and sediments at Station 17 as well as the stations previously mentioned.

Simulations were executed for a range of input parameters to correlate stochastic hydrologic events with mercury distribution patterns and total suspended solid pattern at Station 17. The simulations were analyzed using a range of techniques, primarily comparative schematics of timeseries plots, probability exceedance curves, and load duration curves. The modeling was intended to aid in the development of flow duration curves and mercury loads probability exceedances for selected stations where applicable.

Based on the patterns exhibited throughout various observed and computed probability exceedance curves for flow and mercury, it can be concluded that the model most accurately simulates discharges and mercury loading conditions under high, moist, and mid-range flows. Although mercury loads appear to be attenuated downstream EFPC the same cannot be concluded of BC as it exhibits no significance difference in mercury loading upstream and downstream. Furthermore, results also show that the majority of the mercury in the creek is in the adsorbed form; accentuating the importance of suspended particles and its direct connection to the total mercury concentration in the creek. Even though mercury concentrations during high flood events decreases due to dilution; post hydrological events, the mercury concentration levels are restored. Standard mercury loads probability exceedances were developed based on established limits for the site and a 90.24% reduction in loading appears to be required at Station 17.

The model is intended to serve as a useful remediation tool since the site was characterized using relevant historical records for precipitation, groundwater levels, and river discharges obtained from OREIS and ORNL databases, which were incorporated into the model in the form of boundary or calibration conditions. The incorporation of the ECO Lab module should better characterize the mercury processes in the EFPC environment since mercury species are known to diffuse from contaminated sediment pore water to creek water in the form of diffusive transport.

Improvements can be made to the study in several aspects. For instance, since the study is performed at a watershed scale it might be beneficial to consider the development and implementation of site-specific modeling applications to smaller areas at contaminated buildings and pipes. A more thorough understanding and modeling of the connections between concentrations of inorganic mercury precursors and methylmercury concentration is also needed to better predict future trends of mercury transport at the site. In the thesis related to this research, the EPA water quality limits previously mentioned and based on water usage classification were used to establish a comparison between simulated and recorded mercury loading. An additional recommendation to improve the understanding of the EFPC system is to more specifically apply the model to understand the bioavailability and bioaccumulation in fish in order to establish a more direct connection between water quality and the DOE ROD set fish tissue concentration value of 0.3 milligrams methylmercury per kilogram of wet-weight fish tissue for the site.

Subtask 1.3: Surface Water Flow and Contaminant Transport Model using XPSWMM

- ***Subtask 1.3a: Surface Water Flow and Contaminant Transport Model of ORNL 4500 Area***

SUBTASK 1.3A: RESULTS AND DISCUSSION

- Preliminary research related to this task was carried out during an on-site student internship in collaboration with Eric Pierce at ORNL, to develop a replica of the storm water management system of ORNL’s Outfall 211 and its contributing drainage areas using XPSWMM modeling software in order to assess flood risks. Based on availability of data, modifications to the work scope were made to incorporate:
    - Design storm event routing:
        - 25 year – 24 hour
        - 100 year – 24 hour
        - 500 year – 24 hour
    - Probability of exceedance analysis of outfalls within the domain

- Copies of construction drawings of the area of interest which include buildings 4500N, 4500S, 4501, 4505, 4507, 4508 and 4556 were provided by ORNL engineering personnel. As these buildings were built at different times and stages, it was necessary to conduct an in-depth review of the construction drawings provided to determine how much of the drainage system is still located underground at this time.

- Reviewed a ‘sink and drain’ survey and floor plans via ORNL website in order to compare the number and locations of the storm drains leaving the buildings. Received shapefiles for the area and inserted them into XPSWMM. ArcGIS was used to convert the contours into an xyz file to view the DTM in XPSWMM.

- Developed a water balance model of the areas contributing to Outfall 211 using TSS as a tracer. Issues/Assumptions:

    - ‘New’ ATLAS drawings had inconsistencies.
        - Inlet to the west of MH211-3 was not shown on the drawing.
        - Inlet east of 4500N Wing 1 was shown on the left of the centerline (should be on the right per field reviews).
        - Inlets east of 4500N Wing 2 were either not shown or had no symbol.
        - East storm drain believed to end just east of the MH near 4500N Wing 3 (indicated by old drawings seen from Elizabeth Wright via MapInfo).
    - ArcGIS storm drain files did not contain correct elevation attribute tables.
    - Some inverts, manhole, and inlet elevations were unknown. Reasonable assumptions were made from surrounding or similar data.
    - Assumptions were made for the building area contributing to the roof drains.
    - A single lateral for each building (possibly 2 if needed) was shown in places where there were multiple storm laterals/roof drains because there was an overwhelming amount to begin with. A constant 2 gpm/lateral for condensate and/or cooling water discharging into the system was used. The 2 gpm/lateral was an estimate provided by the ORNL Engineering Department.

- Drew profiles for the 53 link – 52 node network. Input node parameters into the model: Ground elevation (spill crest elevation); Invert elevation. Input link parameters into the model: Diameter; Length; Slope; Manning’s roughness coefficient. Refined the XPSWMM stormwater model by the following revisions: input user inflow for AC units; input stage-stage for Boundary Condition; input infiltration parameters (Horton’s equation); revised Outfall 211 node by adding a storage area held back by a weir prior to its discharge via an orifice.

- Completed a Technical Report of the internship at ORNL outlining the research conducted for this subtask.

- A Master’s thesis is being developed based on the research being carried out for this task and a first draft has been written and submitted for review. An extended thesis proposal was presented and approved by the graduate committee.

- Conducted preliminary calibration of model for steady uniform flow using constant rainfall intensity and currently checking it via mass balance equations. Provided analysis of the water balance for each catchment. Determined the response of the model for a set of Manning’s parameters to simulate the uncertainty in pipe condition, provided comparative runs for one year and determined the probability exceedances for each flow event.

- Conducted preliminary calibration of model for unsteady non-uniform flow where the rainfall intensity varies with time.

    - Data for Outfall 211 was scarce. There was no timeseries information available for Outfall 211; however, there were a few samples (flow rates measured once per day) made available for calibration of the model.

  - The sample taken on May 12, 2009 was chosen for this preliminary calibration where the precipitation for May 11, 2009 and May 12, 2009 was retrieved from the ORNL website. Precipitation near Outfall 211 is monitored by ORNL's Tower C.
  - Obtained 60 min, and 24 hour precipitation data from ORNL's website, generated several models for selected periods of time, and developed inputs for yearly simulations using 60 minute time intervals, and simulations for 1999-2012 using 24 hour time intervals.

- Conducted sensitivity analysis by running multiple simulations of monthly rainfall varying the Manning's n coefficient (0.011-0.017). Refined the model and ran yearly simulations varying Manning's n coefficient and infiltration parameters. The first analysis was for the Manning's coefficient variations (0.011-0.017, 0.035). Pipe 26 (P-26), the last pipe prior to discharging via Outfall 211 (OF-211), was analyzed for comparison. A probability exceedance (PE) curve indicated there were minute variations. Manning's coefficient of 0.014 and the evaporation default of 0.1"/day were held constant for the simulations. The second sensitivity analysis was conducted for various infiltration methods: Green Ampt, Horton, and Uniform Loss.

- A study of contaminant transport within the ORNL area was conducted using the XPSWMM model. The model was run based on the following assumptions:

  1. No loss in the system (i.e. infiltration, evaporation).
  2. Tracer is conservative.
  3. The conservative tracer is added at nodes B-4501 and I-10.1 with constant concentration and flow of 1 mg/L and 0.1 cfs respectively.
  4. 1 year rainfall with 15 minute intervals.
     - Probability distribution function analysis of outfalls within the domain

- These assumptions (1 & 2) were made so that the model's mass balance could be checked or calculated and easily compared to the analytical calculations. The model produced identical results to the analytical calculation results for both tracer mass loading and concentration. This indicates that the model has the capability and potential to be used to study contaminant transport.

- No timeseries data was available for calibration of Outfall 211. ORNL provided monitored data for Outfall 211 during the months of November and December 2012. Dates in which precipitation occurred were noted and actual rainfall data was retrieved off of ORNL's Tower C database and routed through XPSWMM. The results were reviewed and compared to the monitored data. A baseflow of 0.17 cfs was identified. The base flow consists of once-through AC condensate. The four scenarios calibrated achieved successful results.

- Two progress reports have been provided to DOE Headquarters, DOE ORO and ORNL personnel related to this subtask, the first providing information related to the XPSWMM model's preliminary configuration parameters (Milestone 2012-P3-M1.1 submitted 9/14/12) and the second providing preliminary simulation results (Milestone 2012-P3-M1.2 submitted 11/16/12).

SUBTASK 1.3A: CONCLUSIONS

The probabilistic distribution of critical subsurface parameters, such as hydraulic conductivity, porosity, pore size distribution, and storage coefficients were defined specifically for the karst areas. MATLAB's statistical toolbox and scripting tools were used to develop a series of functions for a random generation of distributed hydrologic parameters based on a selected probability density function and statistical parameters. Randomly generated grids were created using the MATLAB toolbox for the uncertainty analysis. Numerical simulations were then conducted for each randomly generated input grid. The output was used to generate daily timeseries for selected hydrological, fate and transport parameters, including groundwater flow velocity at selected points, potential head at selected points, rate of mercury absorption at various locations, concentrations of total mercury at the key stations (EFK 6, EFK 14, EFK 18), total mercury load at the key stations, flux exchange between subsurface and surface. The simulations were used to determine the model uncertainty in terms of stochastic variations of input parameters. Graphical plots of the variation of the output parameters were then used to present the results of the sensitivity analysis, identifying significant parameters and a range of certainty for the model.

- ***Subtask 1.3b: Surface Water Flow and Contaminant Transport Model of Y-12 NSC***

SUBTASK 1.3B: RESULTS AND DISCUSSION

- The study conducted in Subtask 1.3a was carried out to determine the XPSWMM model's capability and potential to be used to study contaminant transport in the ORNL area. Based on the successful results obtained, the same process is being duplicated for the Y-12 NSC.

- A one-dimensional surface water model of the Y-12 NSC was created using XPSWMM. This test model consists of:
    - Runoff mode (70 sub-catchments and 70 nodes).
    - Hydraulics mode (298 nodes and 311 links).

- Much of the data for this study area is currently unavailable due to security restrictions, therefore parameters used in this test model (rainfall data, location and elevation of nodes and pipes, etc.) were assumed. Infiltration was calculated using the Horton method. An imported GIS file was used to locate the outfall locations of Y-12. All the flows were linked to these outfalls. The test model was run for a 24-hr period and the flow at each outfall and pipe generated.

- A draft report of work conducted to date was prepared and serves as a working document which will be continuously updated as data becomes available and results are generated throughout the project period.

- The model was tested with the constant/steady rainfall data.

- The model was conducted with the following assumptions:

- Steady state rainfall.
- No loss in the system (i.e. no infiltration, no evaporation).

- The above assumptions enabled model results to be compared with analytical results in order to verify the calculation capability of the model.

- The model results, assuming steady state rainfall and no loss in the system, were identical to the analytical calculation results (mass balance at the outfall). This indicates that the XPSWMM model has high accuracy and is capable of being used for stormwater management for this site.

- The transport model was tested by injection of an unreactive substance in different nodes using the above assumptions. The model outputs with respect to flow and cumulative mass were comparable to the analytical results. This confirms the calculation capability of the model.

SUBTASK 1.3B: CONCLUSIONS

The model was conducted based on the available data (outfall locations, land use types and contour data from the available GIS files), however, the other important data such as site geometry, the layout of piping system, etc., were not available at this point due to Y-12 NSC security restrictions. Therefore the model was developed in order to test the capability of its calculation by using simple assumptions so that model results could be compared with the analytical results. The results (mass balance) indicated that model has high accuracy and is suitable for use in the stormwater management of the Y-12 NSC plant. Nevertheless the successful results obtained from Subtask 1.3a confirm the capability of model thus the same process is being duplicated for the Y-12 NSC.

To improve model accuracy with respect the Y-12 NSC the following has been proposed:

- Obtain the Y-12 site geometry (if it is possible with the security issue) and use it as input into the model (ground and pipe elevations, pipe sizing, location of outfalls, etc.).

- If site geometry is unavailable, make assumptions of the Y-12 site geometry based on the ground elevation and outfall locations (contour lines) obtained from GIS files. The pipe sizing will also be assumed based on ORNL data.

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TASK 2: SIMULATION OF NPDES- AND TMDL-REGULATED DISCHARGES FROM NON-POINT SOURCES FOR THE EFPC AND Y-12 NSC

INTRODUCTION

The numerical model of the EFPC simulates fate and transport of mercury, conservative tracers and VOC plumes within the EFPC watershed, and assists in analyzing the NPDES and TMDL requirements for surface water and groundwater within the EFPC watershed. The main objectives of this task were to:

- Develop an NPDES and TMDL methodology for analysis of flow and load duration exceedance probabilities for key monitoring stations along Bear Creek and the EFPC from numerical simulations and observed data; and
- Provide analysis of the relative contribution of point and non-point sources to mercury pollution in the watershed including the contributions from the floodplain of the two watershed creeks (EFPC and Bear Creek), the remobilization of stream sediments during stormwater events, the groundwater exchange with the creeks, and the transport within the creeks.

In FY12, FIU utilized the existing EFPC model to provide numerical analysis of contaminant flow and transport within the EFPC and Y-12 NSC watershed and to determine the impact of model parameters on the TMDL. During FY2012 (FIU Year 3), the objective was to determine the effect of the hydrological events (including changes in hydrology caused by D&D activities on the site) on contaminant loading (changes in external and internal loading in time and space), and how imminent ecosystem restoration may affect existing contaminant pools.

The following summarizes the results and conclusions derived from research conducted under this task throughout the FY12 period of performance. Further details are reported in the attached technical report under P3 APPENDIX X: T1T2-001: TASKS 1 & 2 TECHNICAL REPORT which is based on a combination of Task 1 and Task 2 thesis research conducted by students Lilian Marrero, Heidi Henderson and Nantaporn Noosai and have been incorporated as separate subsections of the overall report.

RESULTS AND DISCUSSION

A variety of simulations have been executed with the purpose applying the recently modified model for flow and mercury in developing components of a total maximum daily loads study for the domain area. The objective of developing a TMDL analysis for EFPC is to allocate loads to pollutant sources contributing to the watershed impairment, and consequently, implement appropriate control measures to achieve water quality standards.

In the past, TMDL efforts for the site have included an extensive analysis of recorded water quality data at outfall points regulated by the National Pollutant Discharge Elimination System (NPDES). Efforts associated with this research focused instead on identifying the percent reduction in mercury loading at Station 17 or EFK 23.4 necessary to meet designated water quality criterion.

The model network is shown in Figure 2 below.

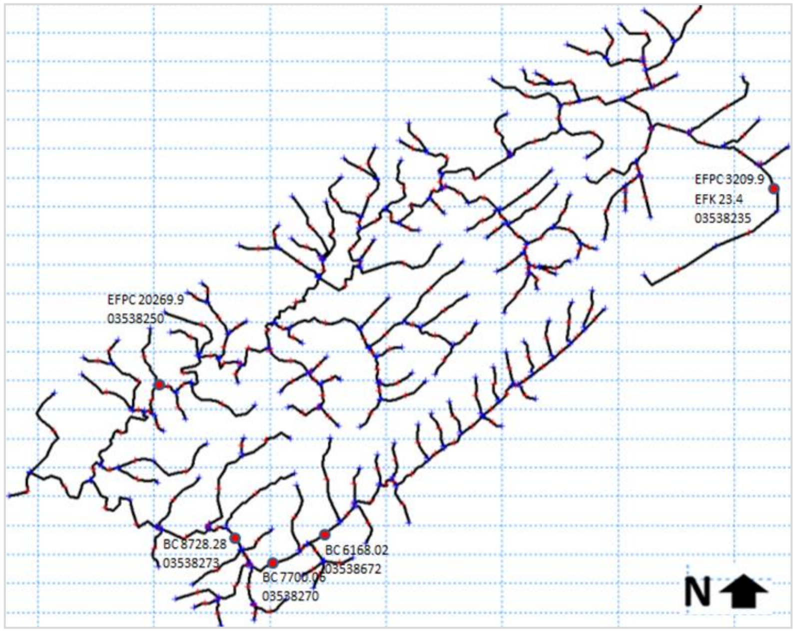


Figure 2. Model network highlighting the stations discussed in the results.

Field stations considered are shown (EFK 23.4, 03538250, 03538273, 03538270, and 03538673) as well as their model computational counterparts (EFPC 3209.9, EFPC 03538250, BC 8728.87, BC 7700.06, BC 6168.82). The discharge and mercury time-series reveal variations in discharge and mercury concentrations at various points throughout EFPC and BC being primarily driven by hydrological events.

Water Quality Module Results

This section describes components of a preliminary TMDL primarily focused on identifying trends in mercury load duration curves and quantifying the percent reduction in loading necessary to meet the water quality criterion mandated for the site based on various water user classifications. TMDL components were developed for EFPC based on available water quality data and the application of the model. In accordance with the approach implemented in previous studies, where applicable, TMDLs, WLAs, and LAs are expressed as the percent reduction in flow or mercury concentrations required to maintain the desired target levels of mercury concentrations in fish tissue.

Designated water use classifications for EFPC encompass a wide range. Among these are the ability to sustain fish and aquatic life, irrigation, livestock watering and wildlife, and recreation. In the case of recreation use, a water quality standard of 51 ppt total mercury concentration in surface water has been suggested by TDEC, EPA, and DOE. For the protection of fish and aquatic life from toxic inorganic substances the State of Tennessee Water Quality Standards suggested a water quality criterion of 770 ppt. There is also the ROD target of 200 ppt for the Station 17 (EFK 23.4) proposed by DOE. A specific water quality criterion has not been designated yet for irrigation, and livestock watering and wildlife designated uses. Water quality criteria for EFPC are summarized in Table 1 below.

Table 1. Mercury concentration limits per designated usage classification

Usage Classification	Mercury Concentration (ppt)
Recreation	51
Fish and aquatic life	770
Irrigation	Not Available
Livestock watering and wildlife	Not Available

The EPA currently recommends a water quality criterion for methylmercury expressed as a fish tissue concentration value of 0.3 milligrams methylmercury per kilogram of wet-weight fish tissue, or 0.3 mg/kg. Per the EPA, a fish tissue residue water quality criterion for methylmercury is more appropriate than a water column-based water quality criterion. However, since the direct link between the EPA’s fish methylmercury water quality criterion and the available water quality mercury concentration data for stations in the watershed were difficult to associate the TMDL comparison was based on the most stringent water quality criterion per usage classification. The most stringent water usage classification was employed and used to establish target levels for TMDL reductions at Station 17.

Time-series of Mercury Concentrations

Simulated mercury time-series are shown in **Figure 3** for computational nodes downstream EFPC and BC that overlap with field stations. Simulated average mercury concentrations for BC at chainage 8728.28, 7700.06, and 6168.82 were 1.6 µg/L, 2.2 µg/L, and 2.9 µg/L, respectively. Mercury concentrations appear to decrease upstream BC. The slightly higher average mercury concentration of 2.9 µg/L computed at BC 8728.28 could be attributed to its proximity to EFPC as previous studies hypothesize on the potential of mercury particulates to be carried downstream during extreme hydrological events. In the case of EFPC, the model initially overestimated the mercury concentration at Station 17 reporting 186 µg/L when the recorded average was 0.89 µg/L. At EFPC 20731.6, the average mercury concentration was 13.7 µg/L. Since EFK 23.4 or Station 17 is the only station with significant mercury data, calibration efforts were thus implemented within the model’s computational dynamics to achieve more realistic results for mercury concentrations at observed Station 17 and computed EFPC 3209.9. **Figure 3** provides visual information about the close match between observed and computed mercury concentration at Station 17 (EFK 23.4).

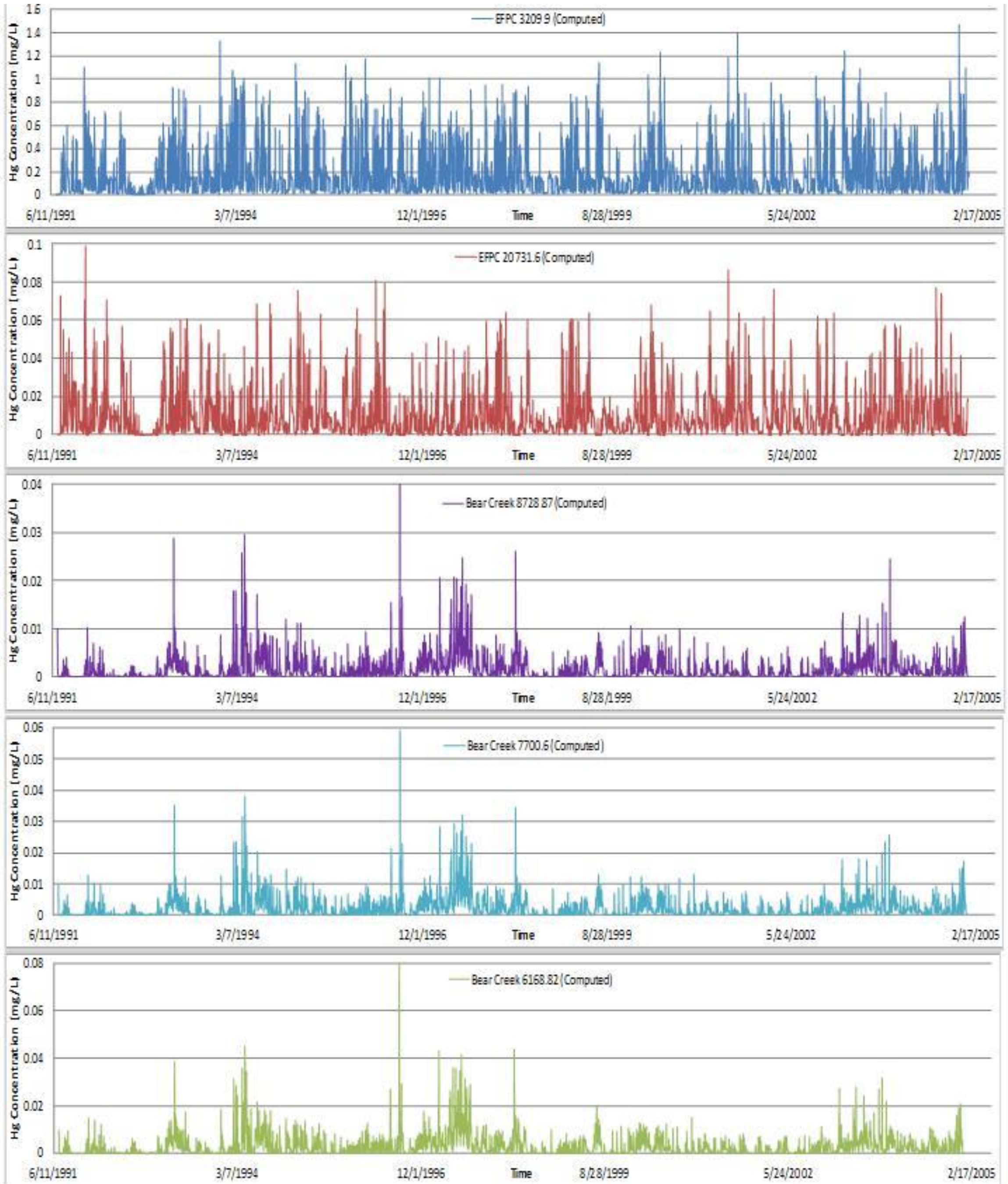


Figure 3. Computed mercury concentrations downstream EFPC and BC for selected model nodes (EFPC 3209.9, EFPC 20731.6, BC 20731.6, BC 8728.87, BC 7700.06, and BC 6168.82).

Figure 4 showcases measured discharges and mercury concentration as a function of time.

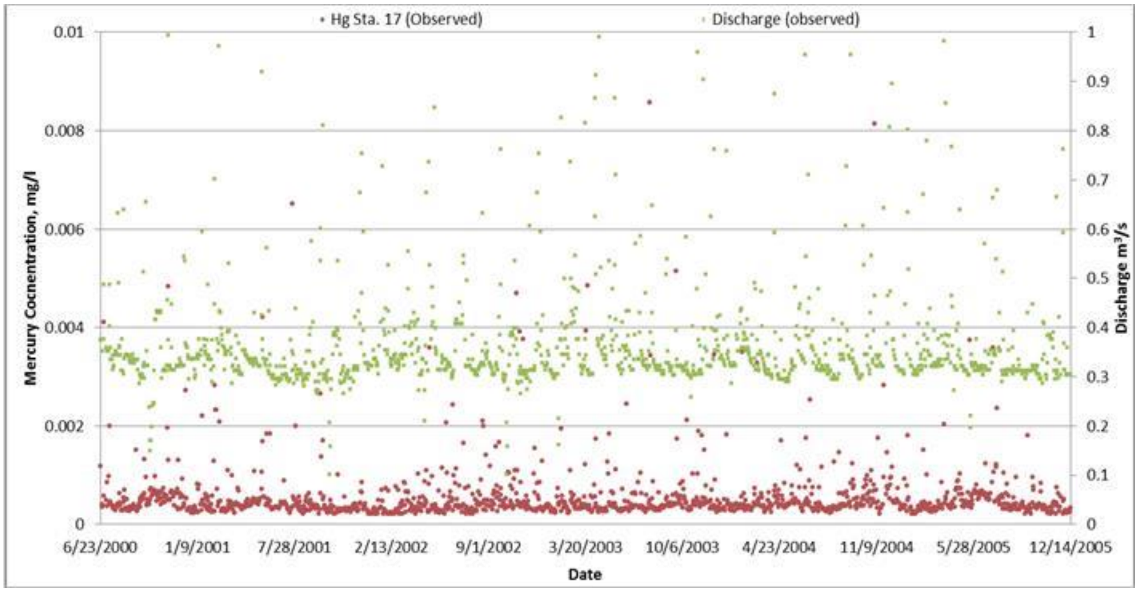


Figure 4. Measured mercury concentrations and discharges at Station 17.

Based on the simulation results, it appears that the majority of the mercury in the creek is in the adsorbed form. As shown in Figure 5, approximately 75.2% of the total mercury is in the adsorbed form and 24.8% is estimated to be present in the dissolved mercury form. A more focused time-series graph is shown in Figure 6 highlighting fluctuations for the year 2000. These results are not only consistent with findings from the Y-12 micro-scale model but are also confirmed by field investigations performed by ORNL in previous years.

This pattern emphasizes the importance of suspended particles and its direct connection to the total mercury concentration in the creek. As shown in Figure 5 and Figure 6, the streambed pore water within the reach contains very high concentrations of dissolved mercury often exceeding 100 ppt. Dissolved mercury in sediment pore water contributes to the high mercury concentration in the creek water through diffusive transport and pore-water recirculation. This occurs as higher flow in the river suspends both the mercury-laden particulates and the highly contaminated trapped water in sediment pores to the creek water. These findings are consistent with studies that associate floodplain with wet weather, high flow events, as oppose to the headwater flux which seem to occur under base-flow conditions.

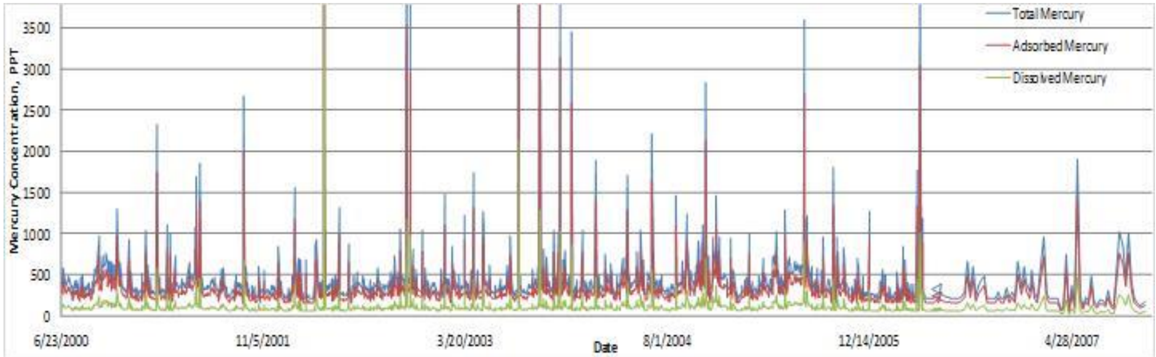


Figure 5. Total, adsorbed and dissolved mercury concentration time-series for the simulated time period starting at year 2000.

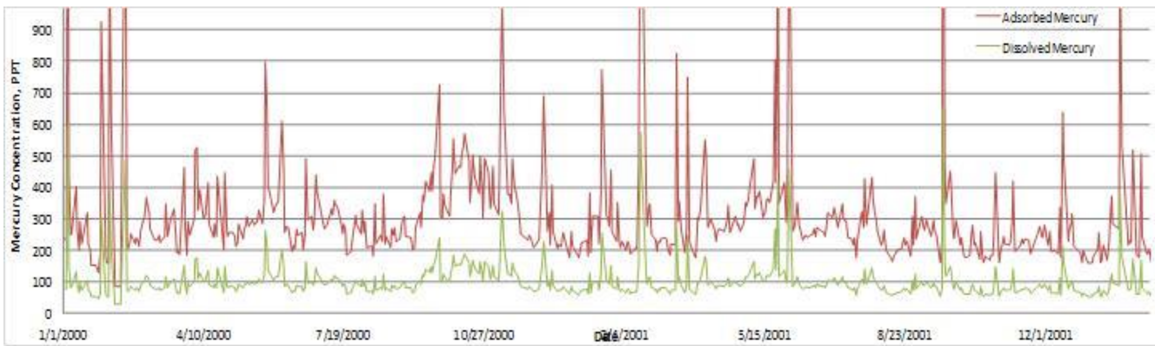


Figure 6. Simulated adsorbed and dissolved mercury concentration time-series for year 2000.

Sensitivity Analysis

The sensitivity of the organic partition coefficient (Kd) within the water quality sorption processes was evaluated to establish how total mercury concentrations computed within the water quality module are impacted by variations of this parameter. The organic partition coefficient parameter was varied. The Kd values used include 0.001 m^3/g, 0.025 m^3/g, 0.050 m^3/g, 0.500 m^3/g, and 5 m^3/g. Figure 7 shows the variability caused by each Kd within the mercury concentration time-series for a 1-year period (2001 - 2002). As shown in the image, the pattern within the time-series is maintained yet the baseline mercury concentration and peak extent is accentuated. The relationship between the organic partition coefficient and the average daily load at Station 17 is best described as logarithmic (Figure 8).

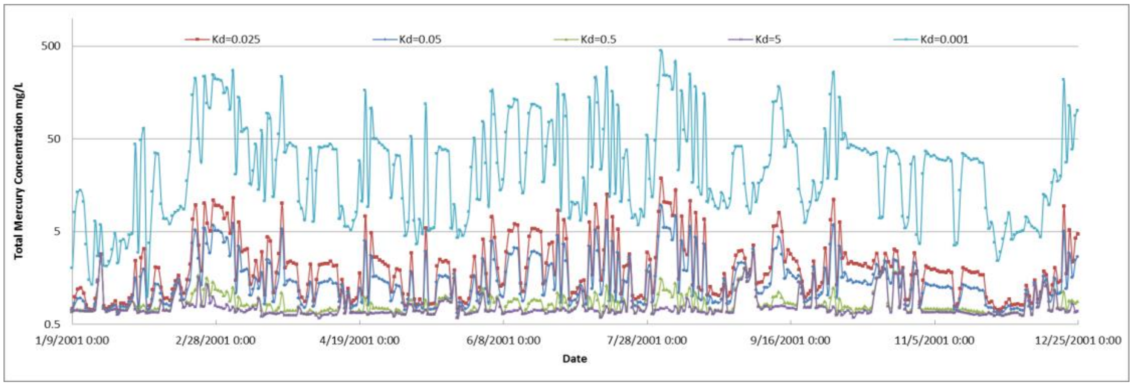


Figure 7. Total mercury time-series depicting sensitivity to organic partition coefficient (Kd) for various simulations.

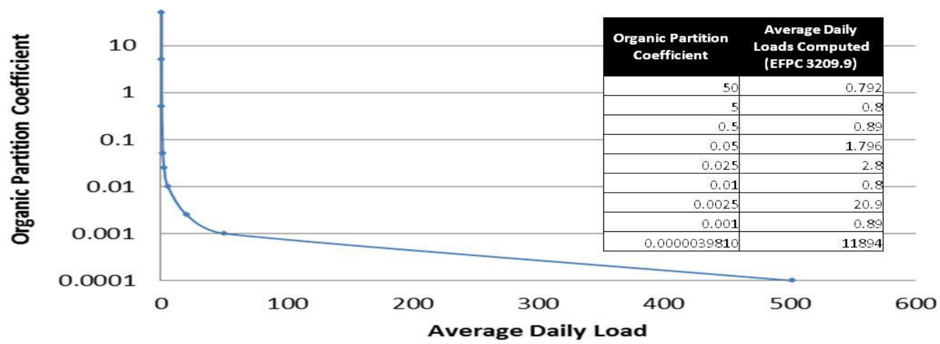
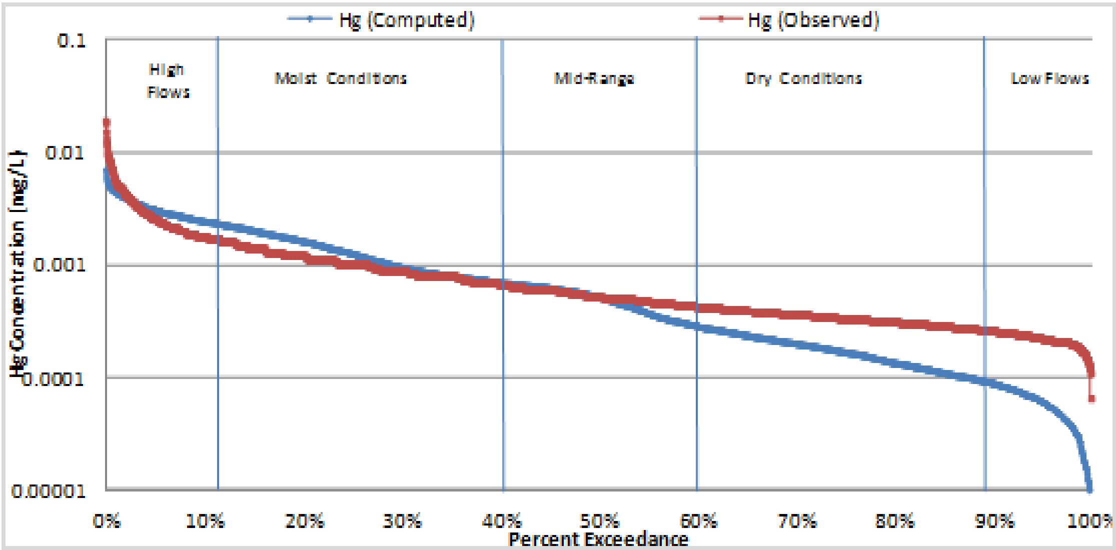


Figure 8. Observed trend between average daily loads and Kd.

Probability Exceedance Calculations for Mercury and TSS

Probability exceedance curves are a classical way for regulators to understand the system in terms of the various flow regimes exhibited. Figure 9 shows the probability exceedances for computed and recorded mercury concentrations prior to the implementation of mercury calibration efforts for EFPC 3209.9 and EFK 23.4. Similarly, Figure 9 depicts the post-calibration mercury concentration probability exceedances for the same station. Figure 9 reveals a much better correlation between the field records and the simulated results at Station 17. As can be observed in Figure 10, the post calibration load was improved by orders of magnitudes.

The daily flow rates and observed concentration were used to obtain daily load estimates in an attempt to identify seasonal trends, compare one location to another, and serve as a future tool for the development of water quality goals. Computed and observed load duration curves (LDCs) were thus created for the previously discussed field records and model stations. These images are shown in Figure 10 through Figure 14. The LDC for model station EFPC 3209.9 and field station EFK 23.4 provides a general trend consistent with the one previously reveal by the FDCs. For the loads, similarly to the discharges, the model is best able to simulate the observed for high flow, mid-range flow, and moist conditions. The mercury loads appear to be attenuated downstream EFPC (Figure 11). This pattern is not of significance at BC (Figure 12) as variations of load duration curves are minor throughout BC. Furthermore, Figure 15 and Figure 16 reveal the differences between recorded and simulated mercury concentrations at Stations 17 before and after the implementation of minor calibration efforts.



Average Concentration (mg/L)	High	Moist	Mid-Range	Dry	Low
Simulated	0.0033	0.0014	0.0005	0.0002	0.0001
Observed	0.0034	0.0011	0.0005	0.0003	0.0002
Averages Difference	0.0001	0.0003	0.0000	0.0001	0.0001

Figure 9. Comparison mercury concentration probability exceedances for EFPC 3209.9 (computed) and Station 17 (observed).

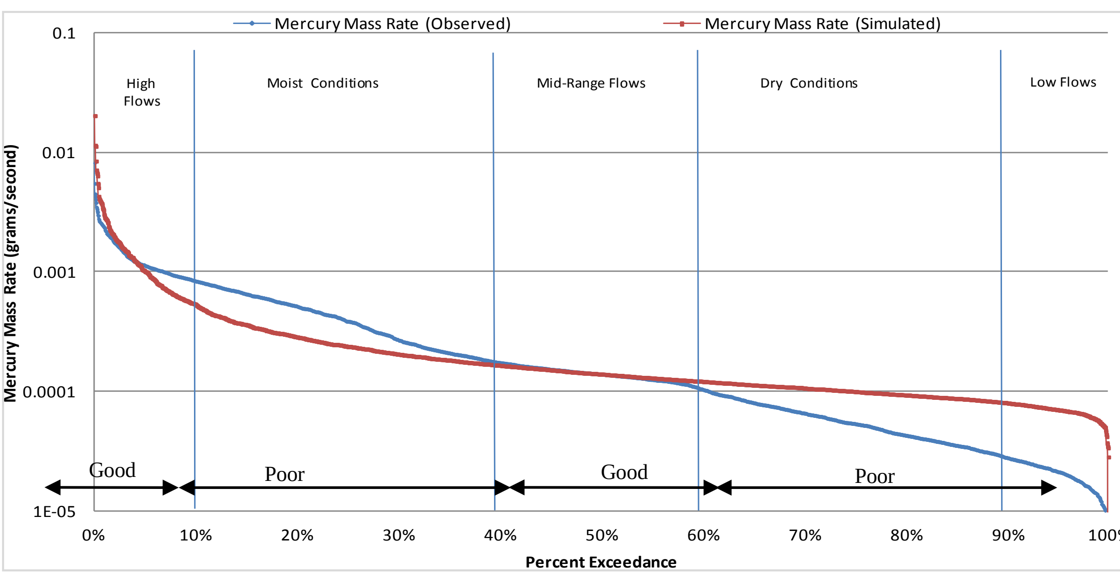


Figure 10. Comparison of load duration curves for EFPC 3209.9 (computed) and EFK 23.4 or Sta. 17 (observed).

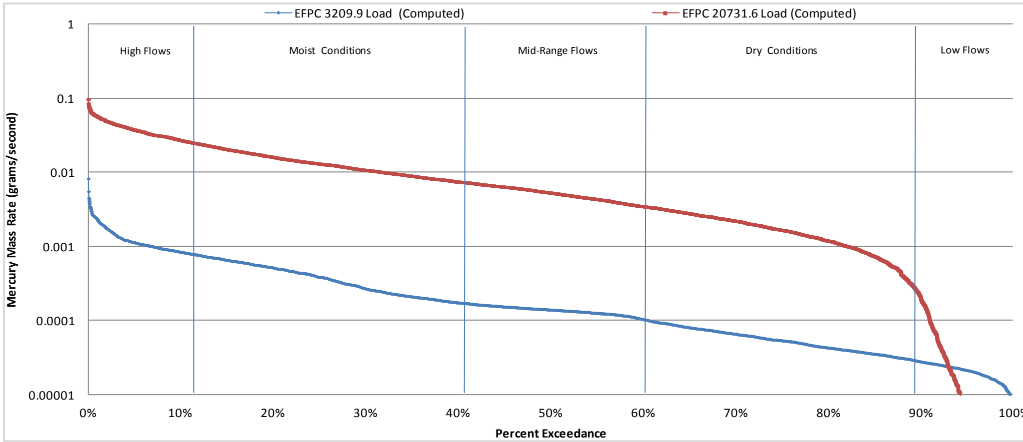


Figure 11. Comparison of load duration curves for computed model stations EFPC 3209.9 and EFPC 20731.6.

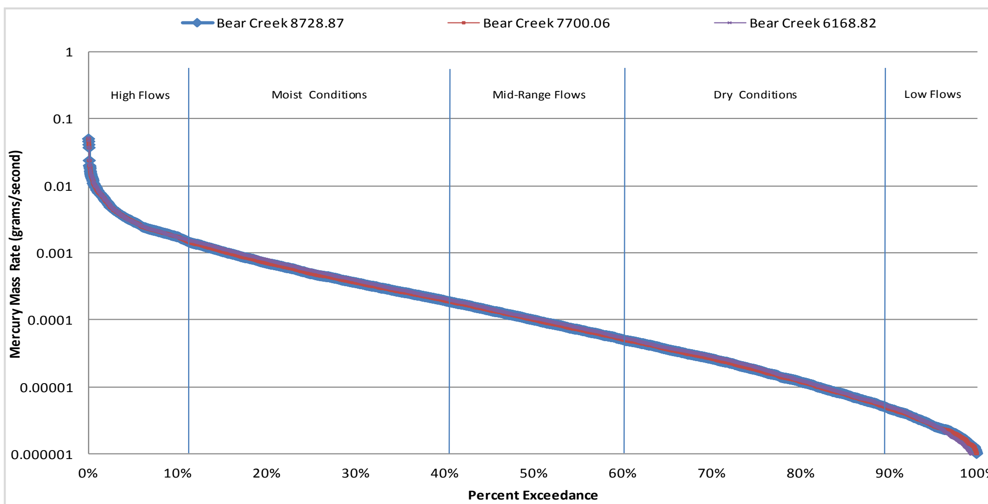


Figure 12. Load duration curves downstream BC.

Total suspended solids patterns were also investigated for Station 17. The same process applied for analyzing the flow and mercury time-series, generating probability exceedance curves, and LDCs were implemented when evaluating total suspended solids. Figure 13. compares recorded and computed TSS and mercury load duration curves for different flow conditions and reiterates the observation established by Figure 5 and Figure 6. The resuspension of mercury-laden fine particulates during high flow conditions (i.e., the wet seasons) plays a significant role in the enhancement of local concentration of mercury along the creek.

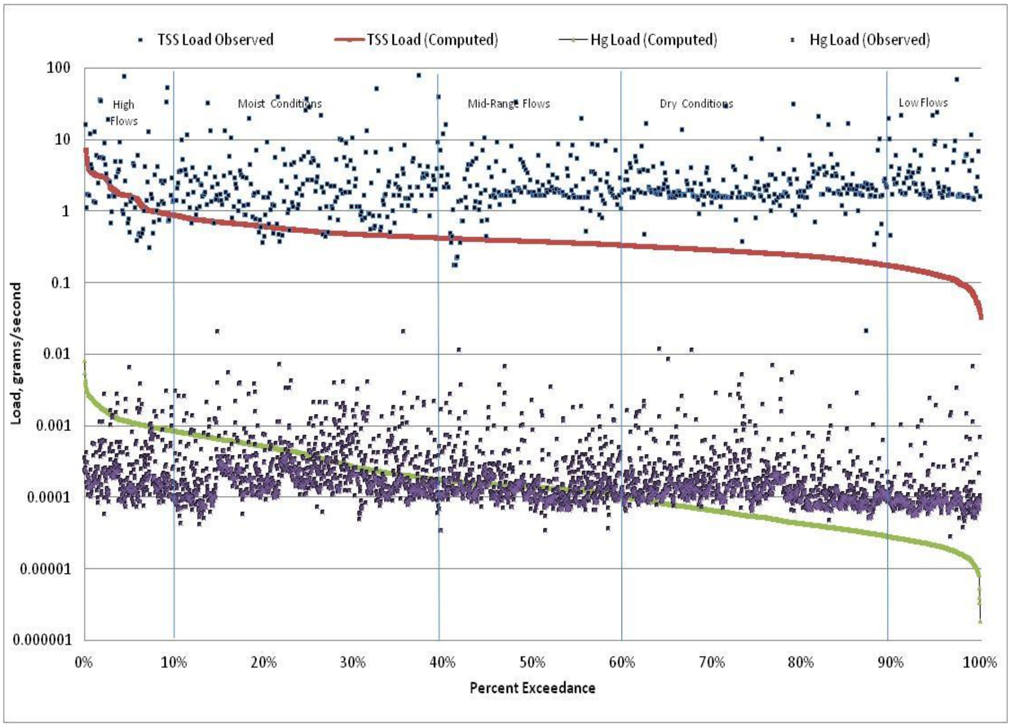


Figure 13. Observed and computed TSS and mercury concentration load for Station 17.

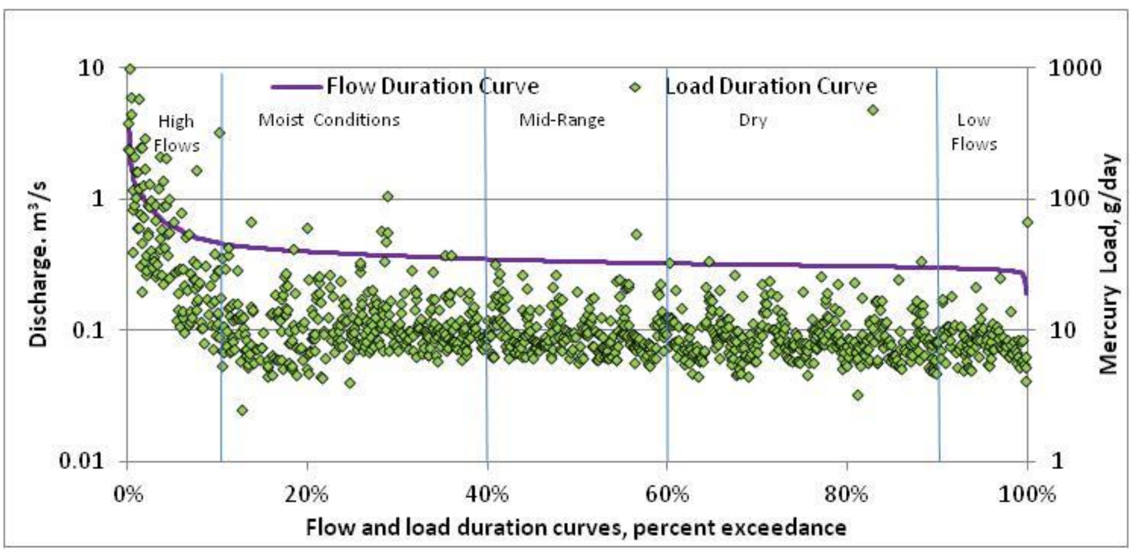


Figure 14. Comparison of flow and load duration curves at Station 17.

Profiles were also generated for the major streams (East Fork Poplar Creek, BC, Gum Hallow Branch, Mill Branch, and Pinhook Branch) in addition to evaluating mercury concentrations and mercury loads downstream EFPC and BC. The profiles were used to analyze fluctuations in mercury concentrations as a function of time and identify how these fluctuations relate to hydrologic events. Figure 15 and Figure 16 portray the simulated mercury concentrations dowstream EFPC per corresponding hydrological event for time-step November 11, 1995 and January 6, 1996. The maximum mercury concentration reached within the simulated period is shown in red. A comparison of the mercury profile downstream the selected branch with the precipitation pattern (Figure 16), reveals that during high flood events mercury concentration decreases due to dilution. However, post hydrological events, the mercury concentration levels increase (Figure 15). At this point, simulation results reveal rainfall as a facilitating agent in the exchange of mercury and its movement through hydrologic zones. The attenuation of mercury concentrations downstream of EFPC is consistent with previous studies.

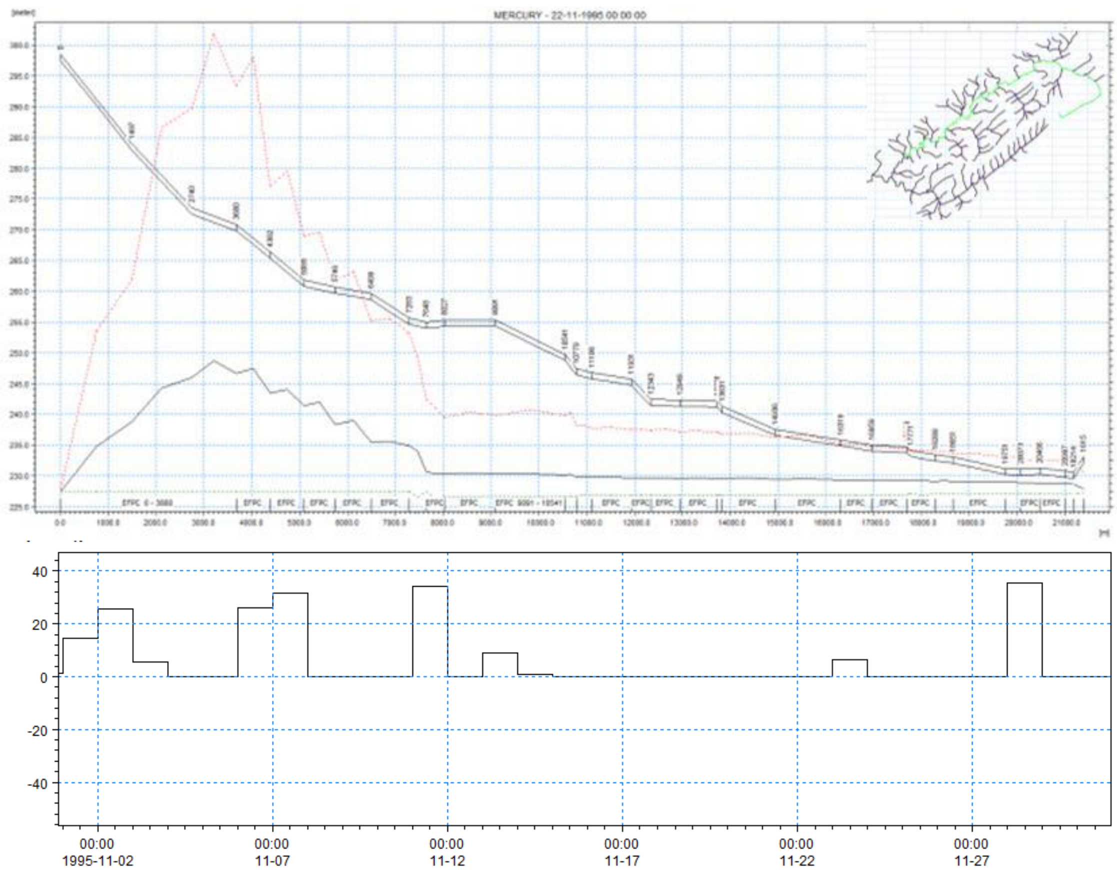


Figure 15. Simulated mercury concentrations downstream EFPC per corresponding hydrological event for November 22, 1995.

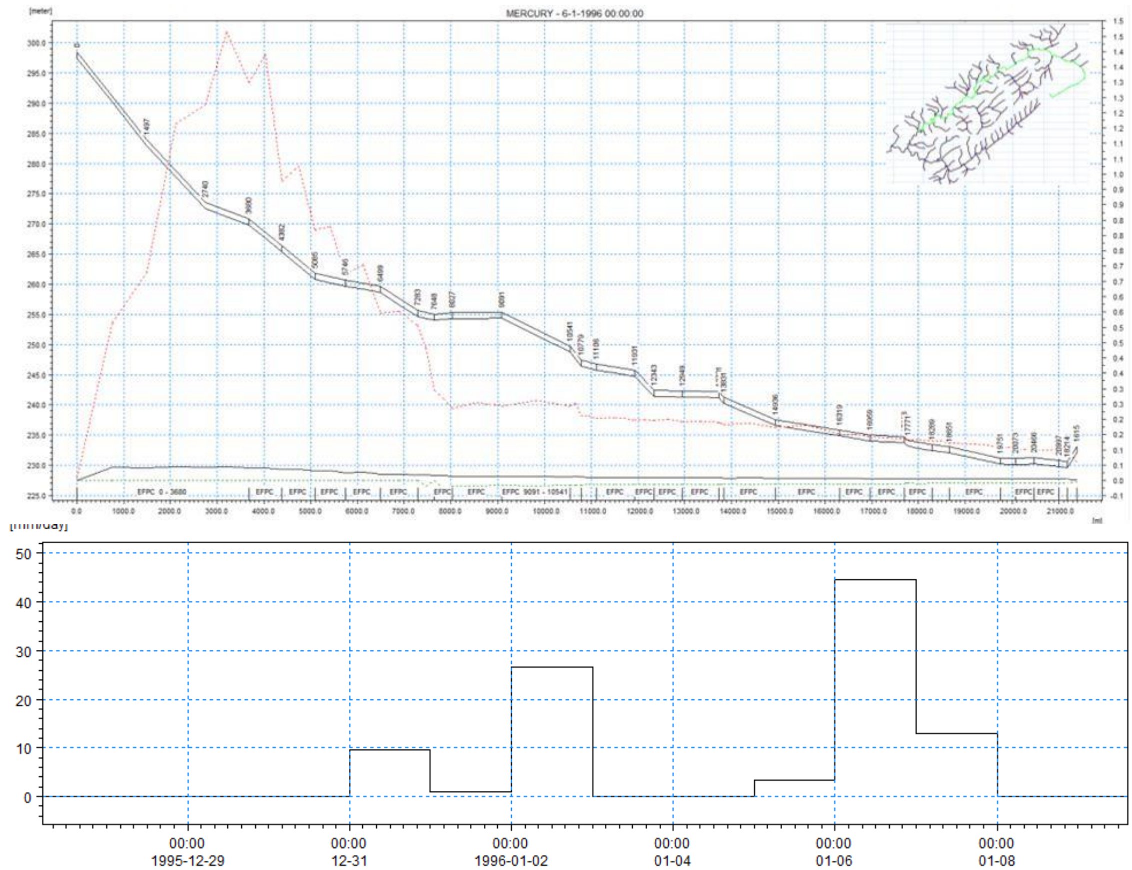


Figure 16. Simulated mercury concentrations downstream EFPC with corresponding hydrological event for January 6, 1996.

Station 17 Target TMDL

The target for the TMDL analyses is the numeric water quality criterion for the pollutant of concern; mercury in this case, for the specified EFPC waterbody. The target concentration was summarized based on the detailed description of water uses and regulations established by EPA, DOE, and TDEC. These numeric water quality targets were translated into TMDLs through the loading capacity or as defined by EPA “the greatest amount of loading received without violating water quality standards”. Several target load-duration curves were generated for EFPC by applying the mercury target concentration of 51, 200, and 770 ppt to each ranked flows used to generate the flow duration curve. These target mercury load duration curves are shown in the figure below. The mercury target maximum load corresponding to each ranked daily mean flow was computed by multiplying the recreation use water quality criterion (51 ppt) by the flow and by the appropriate unit conversion factor. The same calculation was performed for the ROD designated target concentration of 200 ppt and water quality criterion of 770 ppt established to sustain fish and aquatic life.

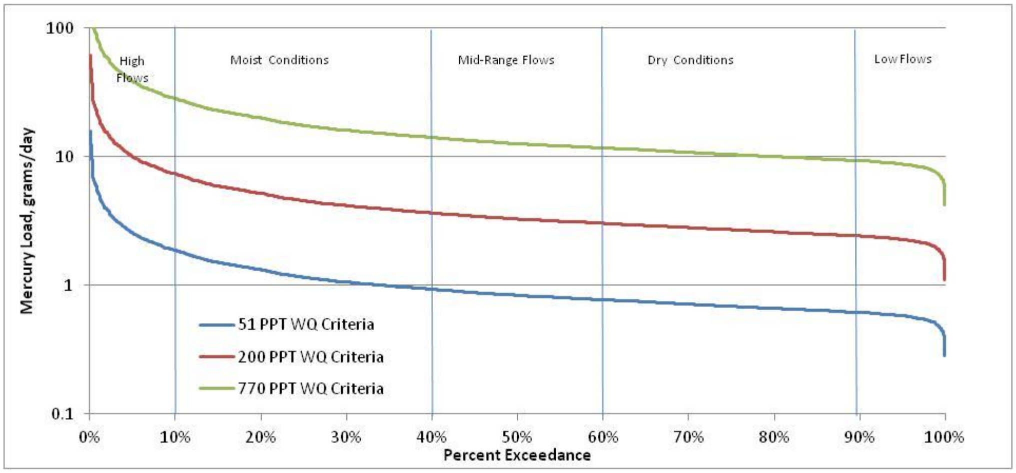


Figure 17. Target mercury load duration curves for 51, 200, and 770 ppt water quality criterion.

Available water quality data for station 17; encompassing a 10 year period, was utilized to compute the percent reduction required to decrease the concentration from the observed mean considering a 95 percent confidence interval (CI) to the desired target level. A total of 2,286 samples were considered. All recorded values were converted to parts per trillion (ppt). All recorded values exceeded the mercury concentration of 51 ppt necessary to meet the recreational use classification. Only 203 of the 2286 samples; in other words, 8.89% of the samples exceeded the 770 ppt criterion required to sustain fish and aquatic life but the majority of the mercury concentrations recorded exceeded the 200 ppt established by the DOE ROD.

Table 2 summarizes the statistical parameters such as the mean, minimum, standard deviation and 95% and 90% confidence interval used in calculating the percent reduction required. The percent reduction was calculated as the difference between the mean and the water quality criteria; considering a confidence interval, and divided by the mean with the incorporated confidence interval. This relationship is shown below by Equation 1.

Table 2. Target TMDL percent reductions at Station 17

No. of Samples	Minimum	Mean	Standard Deviation	Criterion 1	Criterion 2
2286	66.10	495.25	668.91	51	770
No. of Samples Exceeding Criterion 1	**No. of Samples Exceeding Criterion 2**	**95% CI**	**Mean + 95% CI**	**90% CI**	**Mean + 90% CI**
All	203	27.42	522.67	23.01	518.26

$$\%Reduction = \frac{(Mean + Confidence\_Interval) - (Criterion)}{(Mean + Confidence\_Interval)} \qquad \text{(Equation 1)}$$

Based on the equation above, a 90.24% reduction in mercury loading is required at Station 17. Figure 18 shows how the probability exceedance for mercury loading computed from observed flows and mercury concentrations compare to the standard target mercury loading. The average loading at each flow regime is also shown as the dashed red line. Figure 19 also shows the standard water quality criteria compared to the simulated mercury loading for which the required percent reduction was applied. As can be observed from Figure 19 the percent reduction applied places the simulated loading within the range of the 51 ppt water quality criteria and below the 200 ppt standard mandated by the DOE record of decision.

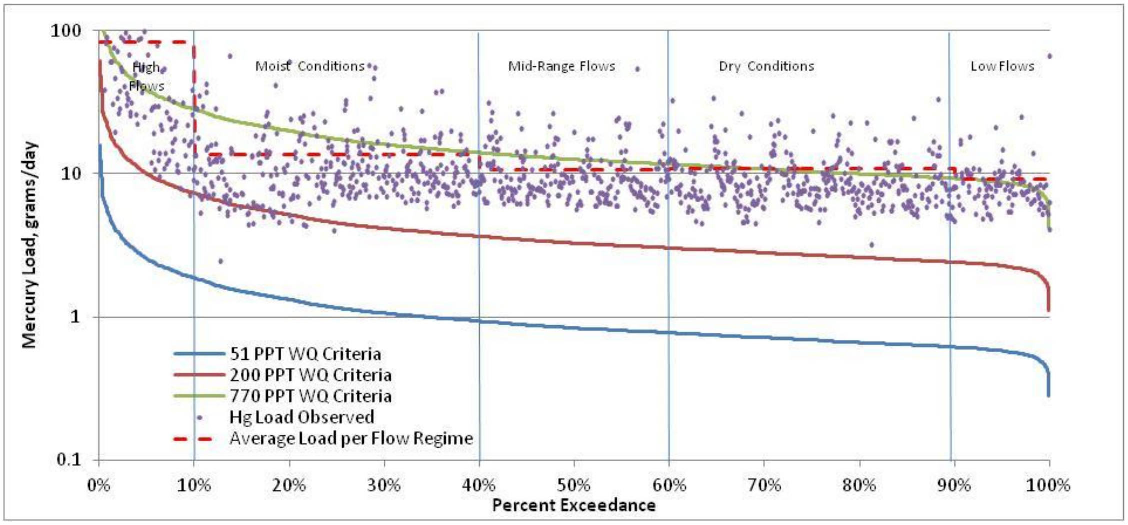


Figure 18. Comparison of target TMDLs and recorded mercury load at station 17.

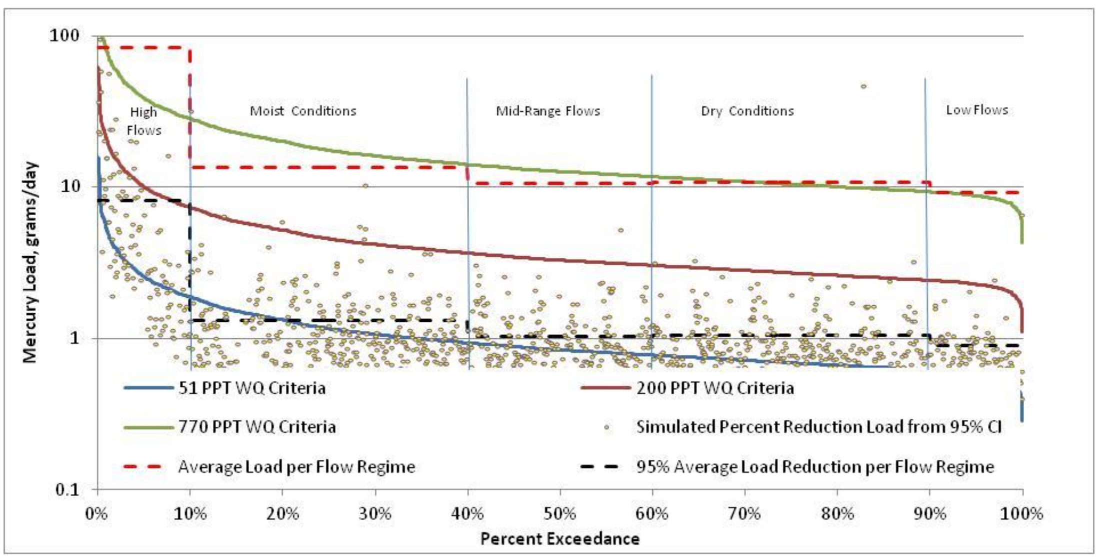


Figure 19. Comparison of simulated mercury loading with applied percent reduction and target TMDLs.

Thermodynamic Simulations to Determine Mercury Behavior in EFPC Water

A report was also prepared for the thermodynamic and the main areas which these simulations covered include:

- *EFPC Test-Bed Simulation*

  The PHREEQC model with enhanced the Hg thermodynamic database was used to predict the distribution of Hg species, Hg species and mineral saturation index sensitivity to water pH and temperature. The EFPC water quality data was obtained from Dong et al. (2010).

- *Hg Speciation Distribution*

  The EFPC Hg species distribution using the improved PHREEQC model and the EFPC water quality data is shown in Figure 20.

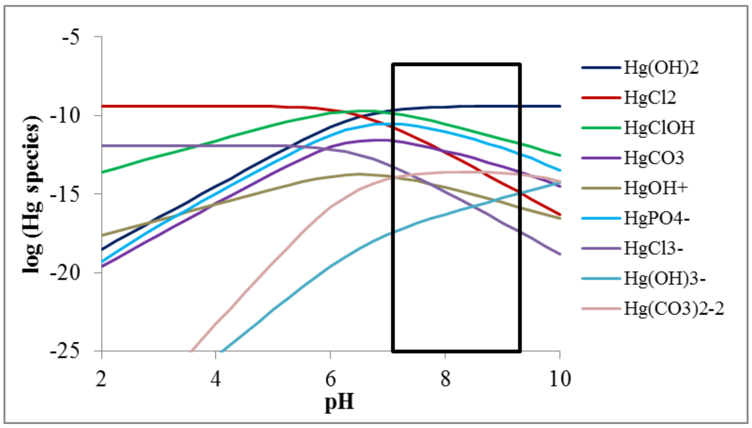


Figure 20. Hg species distribution in EFPC water.

The $Hg(OH)_2$ is the dominant species at the typical EFPC water pH (black box shown in Figure 20, pH ~ 7-9.2). The second dominant species, HgClOH. $Hg(OH)_2$, is low at low pH while $HgCl_2$ dominates at low pH (0-6). $Hg(OH)_2$ concentration increases with water pH (0-6) while $HgCl_2$ decreases. The concentration of $Hg(OH)_2$ at high pH is expected since the OH amount which is available for Hg binding increases with the water pH, thus the high $Hg(OH)_2$ concentration at high water pH is obtained.

- *Sensitivity on Water Temperature and Water pH on Hg Speciation*

  The sensitivity of EFPC Hg speciation to water temperature and pH were studied at temperature 5-35 °C and pH 2-10. The calculations showed that the formation of Hg-OH and Hg-CO_3 species increase with increase in water temperature, while the increase in water temperature does not favor the formation of Hg-Cl species. Increase in water pH increases the formation of $Hg(OH)_2$ and $Hg(OH)_3^-$, however for $Hg(OH)^+$, HgOHCl, and $HgCO_3$, the concentrations increase with water pH between 2-7, then a decline in their concentrations are observed at pH > 7. Low water pH (pH 2-6) does not influence the Hg-Cl concentration; however, a decrease in its concentration is obtained at pH > 6.

- *Sensitivity to Water Temperature and pH on Mineral Precipitations*

  Sensitivity analyses of water temperature and pH on the mineral precipitations under EFPC water conditions were conducted at a temperature range of 5-35 °C and for water pH 2-10. The calculations demonstrated the effect of water temperature and pH on the SI of dominant precipitated minerals in EFPC water. The SI of Ferrihydrite, Goethite, Magnesioferrite, and Hematite was observed to increase with water temperature; however temperature did not affect the formation of FCO_3Aptite, Lepidocrocite, Hydroxylapatite, and Arogonite. Increase in water pH favors the formation of all the aforementioned minerals such that their SIs are increased with water pH. At EFPC water conditions of pH 7-9.2 and temperature 25 °C, water is supersaturated with Ferrihydrite, Goethite, Magnesioferrite, Hematite, FCO_3Aptite, Lepidocrocite and Hydroxylapatite, and the precipitation of these minerals was expected. At pH 8, the EPFC water was saturated with Arogonite and its precipitation was obtained at pH > 8.

CONCLUSIONS

The objectives of this study were met through the successful integration of the ECO Lab module to enhance the simulation of mercury transport and in the demonstration of the application of the model to the mercury TMDL analysis for the project site in the EFPC watershed.

Modeling software MIKE SHE, MIKE11, and ECO Lab were thus combined in a comprehensive package that models the flow and transport of mercury in exchange with sediment. The application of the enhanced models includes an analysis of spatial and temporal patterns stimulated by variations of selected properties of the sub domain. The impact of sedimentation on the fate of mercury was assessed through a series of simulations and using the sedimentation layer module (ECO Lab); this module addresses the dissolved mercury in the water, the adsorbed mercury concentration on suspended matter, the dissolved mercury in sediment pore water, and the adsorbed mercury in the sediment.

In the application of the model to the EFPC watershed, previous modeling efforts, which originally included only the upper portions of EFPC, were extended to include the entire EFPC, down to station EFK 6.4 and the BC. The model is capable of simulating the entire hydrological cycle. Water quality, transport, and sediment related parameters were updated based on DOE experimental reports and journal publications to include observed data of flow, stage, and mercury concentrations in soil, surface water, groundwater and sediments at Station 17 as well as the stations previously mentioned.

Simulations were executed for a range of input parameters to correlate stochastic hydrologic events with mercury distribution patterns and total suspended solid pattern at Station 17. The simulations were analyzed using a range of techniques, primarily comparative schematics of time-series plots, probability exceedance curves, and load duration curves. The modeling was intended to aid in the development of flow duration curves and mercury loads probability exceedances for selected stations where applicable.

Based on the patterns exhibited throughout various observed and computed probability exceedance curves for flow and mercury, it can be concluded that the model most accurately simulates discharges and mercury loading conditions under high, moist, and mid-range flows. Although mercury loads appear to be attenuated downstream EFPC the same cannot be concluded of BC as it exhibits no significance difference in mercury loading upstream and downstream. Furthermore, results also show that the majority of the mercury in the creek is in the adsorbed form; accentuating the importance of suspended particles and its direct connection to the total mercury concentration in the creek. Even though mercury concentrations during high flood events decreases due to dilution; post hydrological events, the mercury concentration levels are restored. Standard mercury loads probability exceedances were developed based on established limits for the site and a 90.24% reduction in loading appears to be required at Station 17.

The model is intended to serve as a useful remediation tool since the site was characterized using relevant historical records for precipitation, groundwater levels, and river discharges obtained from OREIS and ORNL databases, which were incorporated into the model in the form of boundary or calibration conditions. The incorporation of the ECO Lab module should better characterize the mercury processes in the EFPC environment since mercury species are known to diffuse from contaminated sediment pore water to creek water in the form of diffusive transport.

Improvements can be made to the study in several aspects. For instance, since the study is performed at a watershed scale it might be beneficial to consider the development and implementation of site-specific modeling applications to smaller areas at contaminated buildings and pipes. A more thorough understanding and modeling of the connections between concentrations of inorganic mercury precursors and methylmercury concentration is also needed to better predict future trends of mercury transport at the site. In the thesis research related to this task, the EPA water quality limits previously mentioned and based on water usage classification were used to establish a comparison between simulated and recorded mercury loading. An additional recommendation to improve the understanding of the EFPC system is to more specifically apply the model to understand the bioavailability and bioaccumulation in fish in order to establish a more direct connection between water quality and the DOE ROD set fish tissue concentration value of 0.3 milligrams methylmercury per kilogram of wet-weight fish tissue for the site.

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TASK 3: PARAMETERIZATION OF MAJOR TRANSPORT PROCESSES OF MERCURY SPECIES

INTRODUCTION

The overall objective of this task is to provide laboratory investigation of critical mercury transport, transformation, and exchange processes (i.e., methylation/demethylation, adsorption/desorption, and dissolution/precipitation) that are important in the numerical flow, transport and chemical reaction models. The laboratory experimental work provides insight on parameters relevant to the Oak Ridge Reservation (ORR) and which are required in the numerical model, such as dissolution rate of mercury and the proportion of mercury species available for methylation/demethylation in sediments. In addition, experimental work will aid in the analysis of the effect of significant environmental factors (e.g., pH, Eh, sunlight) on the major transport and transformation processes of Hg.

Our previous studies have revealed that: 1) the percentage of Hg species available for methylation or demethylation is a critical parameter for evaluating the production and degradation of MeHg in aquatic ecosystems, 2) under certain environmental conditions, dissolution of mercury sulfide (cinnabar) can significantly increase aqueous Hg concentrations, which in turn could increase the proportion of Hg with increased mobility, reactivity, and bioavailability, and 3) thiol-containing compounds, probably through acting as complexing ligands, may enhance cinnabar dissolution in which process the adsorption of aqueous Hg species released from cinnabar plays an important role. The scope of work in FY13 for this task therefore placed a special focus on understanding the dissolution process of mercury sulfide in soil and sediment. A series of studies were conducted to:

- Develop new analytical techniques, particularly isotope tracer and isotope dilution methods, for identification and quantification of important Hg species to better study not only the dissolution of mercury sulfide but also the other transport and transformation of Hg cycling.

- Investigate the dissolution of mercury sulfide by using a comprehensive way through simultaneously considering multiple reactions and environmental factors (e.g., pH, Eh, ligands) relevant to mercury sulfide.

- Provide an improved understanding of the process of mercury sulfide dissolution by comparing studies of theoretical calculations and experimental work, in particular on the role of thiol-containing ligands on mercury sulfide dissolution.

The following summarizes the results and conclusions derived from research conducted under this task throughout the FY12 period of performance. Further details are reported in the attached technical report under P3 APPENDIX XI: T3-001: TASK 3 TECHNICAL REPORT.

RESULTS

Development of the Isotope Dilution (ID) Method for Analyzing Inorganic Hg Concentration in Water

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

As shown in Figure 21, a Flow Injection System (FIAS 400) was successfully coupled to ICP-MS and it could be used to analyze mercury isotopes in samples. Influence of nebulizer gas flow rate (0.5 L/min, 0.6 L/min, 0.8 L/min, 0.96 L/min) on the sensitivity was tested. 0.8L/min was chosen as the flow rate of nebulizer gas.

Figure 21. Coupling of a Flow Injection System (FIAS 400) to ICP-MS for analyzing mercury isotopes.

- ***Development of the isotope dilution method for analyzing inorganic Hg concentrations in water***

Prior to analysis of the water sample, a certain amount of ^{199}Hg was added to samples to form a final concentration of 10 ppt. Concentrations of Hg^{2+} in samples were then calculated according to Eq. 1. The method detection limit was estimated to be 6.7 ppt.

$$C_s = \frac{C_{199}A_{199}^{202} - RC_{199}A_{199}^{199}}{RA^{199} - A^{202}} \qquad (1)$$

R: ratio of $^{202}Hg^{2+}$ to $^{199}Hg^{2+}$ in samples

C_s : the concentration of Hg in samples.

C_{199} : concentrations of spiked ^{199}Hg.

A_{199}^{199} : the abundance of ^{199}Hg in ^{199}Hg.

A_{199}^{202} : the abundance of ^{202}Hg in ^{199}Hg.

A^{199} : the abundance of ^{199}Hg in natural Hg.

A^{202} : the abundance of ^{202}Hg in natural Hg.

Development of the Isotope Dilution (ID)-Phenylation-Purge and Trap-ICP-MS Technique for Analyzing Organomercury Species

An isotope dilution method was developed for accurate analysis of MeHg and EtHg in environmental samples. To water samples 100 µl 167.8 ng/L $Me^{200}Hg$ and 100 µl 168.6 ng/L $Me^{199}Hg$ was added. $Me^{202}Hg$, $Me^{200}Hg$, $Me^{199}Hg$, $Me^{201}Hg$, $Et^{202}Hg$, $Et^{200}Hg$, $Et^{199}Hg$, and $Et^{201}Hg$ were detected using phenylation-purge and trap-ICP-MS technique (Figure 22). Concentrations of MeHg and EtHg in water sample could be calculated by the ratio of $Me^{202}Hg$/ $Me^{200}Hg$ according to Eq. 2. and $Et^{202}Hg$/ $Et^{199}Hg$ (Eq. 3), respectively. The concentrations of MeHg and EtHg (spiked) in water samples were measured to be 0.11±0.004 ng/L and 0.20±0.002 ng/L, with a good reproducibility (RSD<5%). The developed method was then validated by analyzing MeHg and EtHg (spiked) in reference sediment (IAEA 405) and fish materials (DORM 4). The recoveries of EtHg in IAEA 405 and DORM 4 were 104.1±3.3% for IAEA 405 and 99.7±2.7% for DORM 4. The recovery of MeHg was 103.3±3.2% and 106.9±0.98%, respectively. RSDs of the measured concentrations of MeHg and EtHg in sediment and fish samples were also lower than 5%, indicating the high precision of the developed method.

$$C_s = \frac{C_{200}A_{200}^{202} - RC_{200}A_{200}^{200}}{RA^{200} - A^{202}} \qquad (2)$$

R: ratio of $Me^{202}Hg$ to $Me^{200}Hg$ in samples

C_s : the concentration of MeHg in samples.

C_{200} : concentrations of spiked $Me^{200}Hg$.

A_{200}^{200} : the abundance of ^{200}Hg in $Me^{200}Hg$.

A_{200}^{202} : the abundance of ^{202}Hg in $Me^{200}Hg$.

A^{200} : the abundance of ^{200}Hg in natural Hg.

A^{202} : the abundance of ^{202}Hg in natural Hg.

$$C_s = \frac{C_{199}A_{199}^{202} - RC_{199}A_{199}^{199}}{RA^{199} - A^{202}} \quad (3)$$

R: ratio of Et^{202}Hg to Et^{199}Hg in samples

C_s : the concentration of EtHg in samples.

C_{199} : concentrations of spiked Et^{199}Hg.

A_{199}^{199}: the abundance of ^{199}Hg in Et^{199}Hg.

A_{199}^{202} : the abundance of ^{199}Hg in Et^{199}Hg.

A^{199} : the abundance of ^{199}Hg in natural Hg.

A^{202} : the abundance of ^{202}Hg in natural Hg.

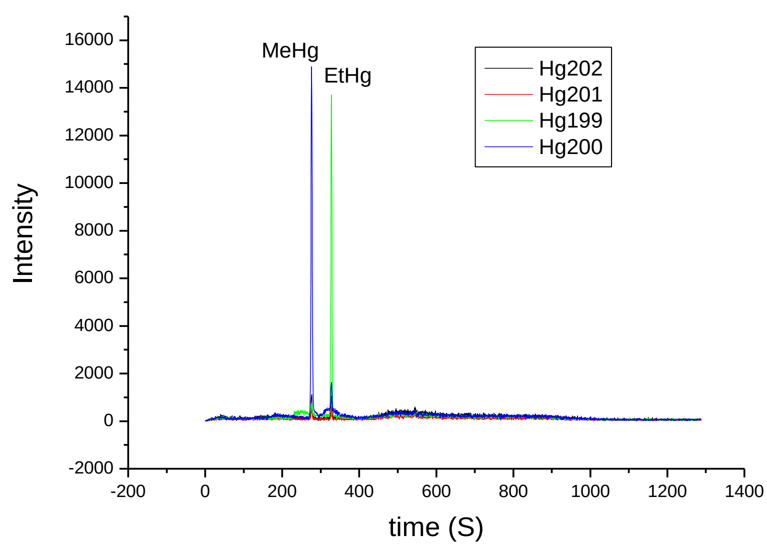

Figure 22. Typical chromatogram of pool water sample spiked with Me200Hg and Et199Hg and analyzed by aqueous phenylation followed by purge and trap-ICP-MS.

Role of Thiol-containing Substances in Cinnabar Dissolution

Selected ligands, including both with and without thiol group in molecular structure, were investigated for the role they play during cinnabar dissolution. As shown in Figure 23, thiol group plays an important role in cinnabar dissolution, as evidenced by the fact that Hg^{2+} released from cinnabar in 10μM L-cysteine was observed to be 40~60 times higher than that in 10μM of L-serine. The only molecular structure difference between L-serine and L-cysteine is that the former contains a hydroxyl functional group at the beta carbon whereas the latter contains a thiol group at the same position. These results confirm the critical role of thiol group in enhancing mercury sulfide dissolution. In fact, the enhancing effect of L-serine on mercury sulfide dissolution is minimal, as it released a similar amount of Hg from cinnabar as sodium nitrate did in the control experiments (Figure 23).

Although GSH contains thiol group as well, its enhancing effect on mercury sulfide dissolution seems much weaker than that of L-cysteine. Concentrations of released Hg (II) from cinnabar were analyzed to be 9.1±1.4, 11.4±3.1 and 116.6±1.7 μg L^{-1} in the presence of in 10 μM of GSSG, GSH and L-cysteine, respectively. Total concentration of Hg released from cinnabar in the presence of GSH was only about 10% of that in the presence of L-cysteine. Hg^{2+} released in the presence of GSSG was slightly less than that in the presence of GSH (Figure 23).

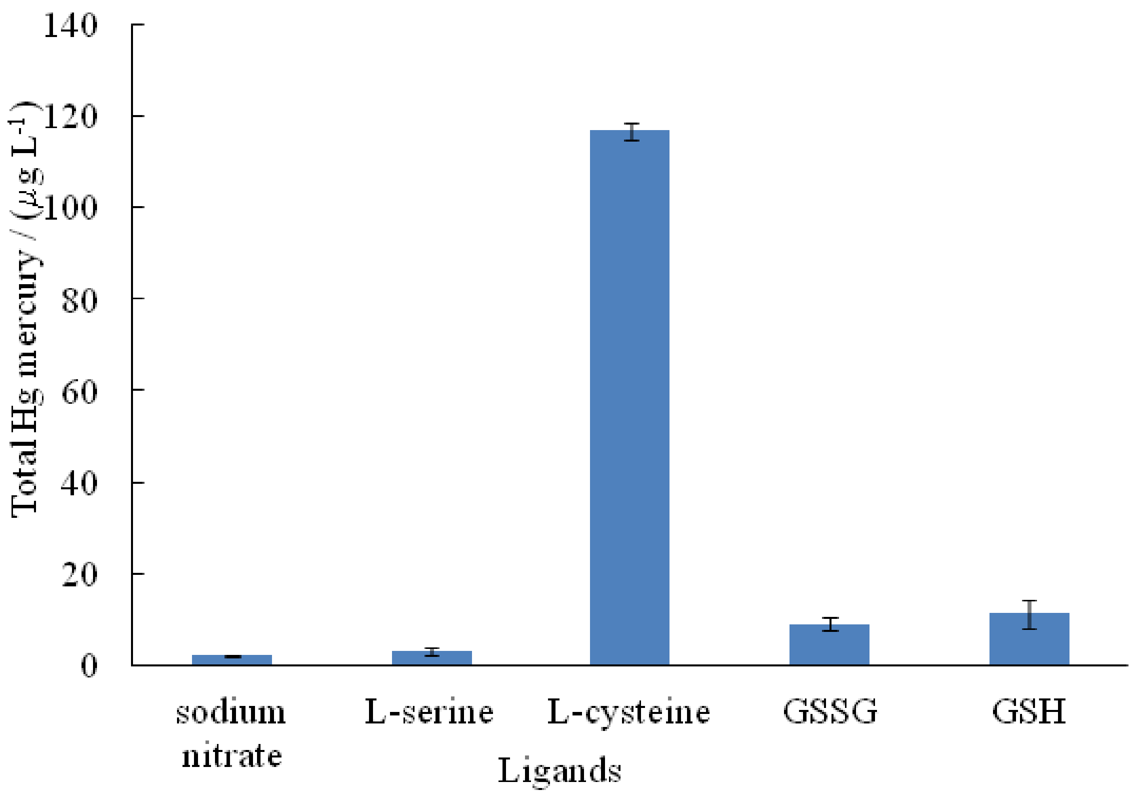

Figure 23. Effect of thiol group on the release of dissolved Hg from cinnabar.

Role of Dissolved Oxygen in Cinnabar Dissolution

The measured total Hg concentration released from cinnabar at pH 8.0 without the presence of ligands increased with the levels of dissolved O_2 and reached 2.1 µg L^{-1} within 24 h in saturated O_2 medium (Figure 24). This value was much higher than that in anaerobic condition (~0.1µg L^{-1}), indicating the role of sulfur oxidation by O_2 in enhancing HgS dissolution.

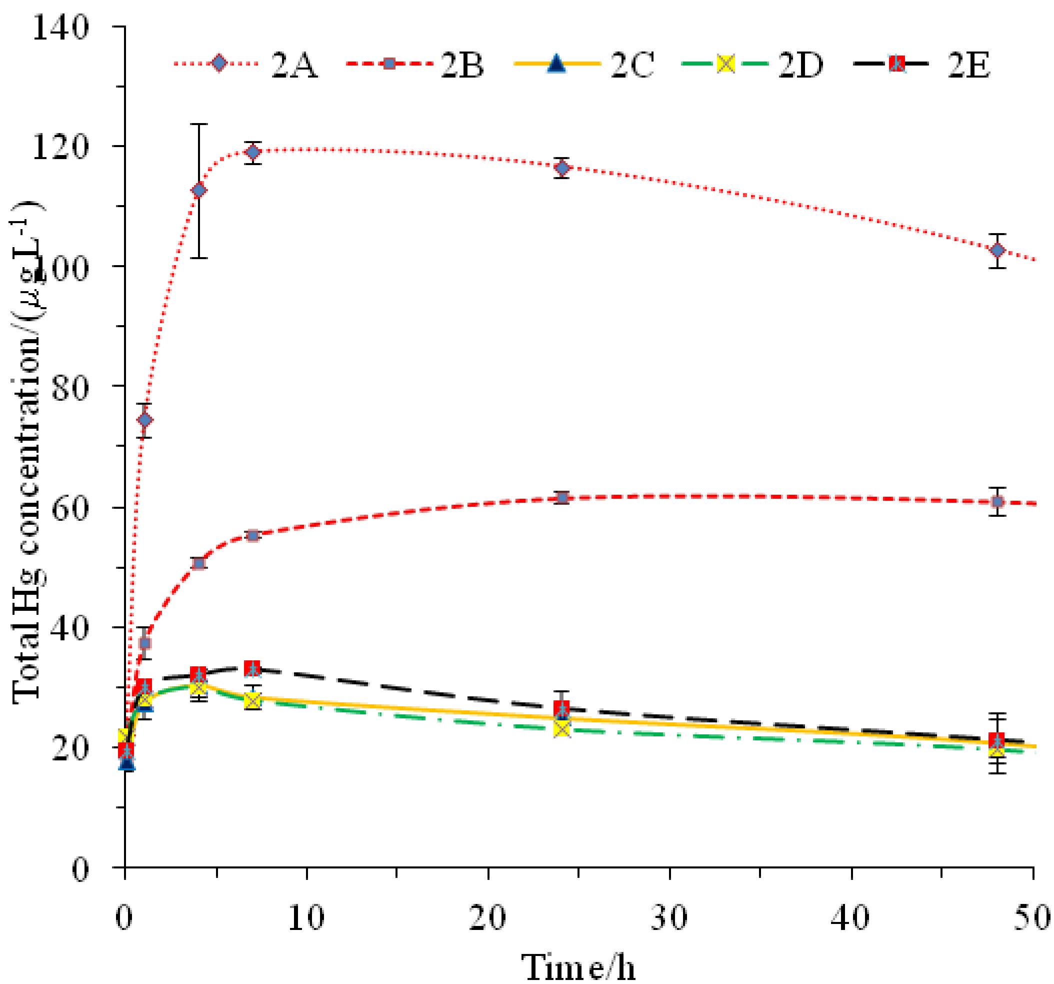

Figure 24. Effects of dissolved oxygen on the thiol-involved release of Hg(II) dissolved from cinnabar. 2A. Saturated oxygen dissolution; 2B. Dissolution open to the atmosphere; 2C. Anaerobic dissolution with L-cysteine solution (10 µM, pH 8.0) being purged by nitrogen for 1 hr before it was mixed with cinnabar; 2D, Anaerobic dissolution with L-cysteine solution (10 µM, pH 8.0) being purged by nitrogen for 5 hrs; 2E Anaerobic dissolution with L-cysteine solution (10 µM, pH 8.0) being purged by nitrogen for 21 hrs.

CONCLUSIONS

The dissolution of mercury sulfide is a complicated process and needs to be carefully investigated by simultaneously considering multiple reactions and environmental factors.

Thiol-containing ligands (e.g., cysteine) play an important role in promoting mercury sulfide dissolution which at the same time is controlled by other factors such as dissolved oxygen.

The process of mercury sulfide dissolution in soil and sediment is a critical step during the biogeochemical cycling of mercury, as this process governs the mobility and bioavailability of important mercury species.

FUTURE WORK

The speciation of mercury released from the dissolution of mercury sulfide needs to be extensively studied through theoretical calculations, chromatographic separations, and/or spectroscopic techniques, as the mobility, reactivity, and bioavailability of mercury are controlled by speciation.

The reactivity of mercury species released from mercury sulfide dissolution relevant to important mercury transformation processes such as oxidation/reduction and methylation/demethylation needs to be investigated to further understand the role of mercury sulfide dissolution in the biogeochemical cycling of mercury.

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TASK 4: GEODATABASE DEVELOPMENT FOR HYDROLOGICAL MODELING SUPPORT

INTRODUCTION

During 2007-2011, FIU developed three integrated watershed models for Y-12 NSC, White Oak Creek (WOC), and EFPC which include overland, stream and groundwater flows in the variable and fully saturated zones, and implement the complex biological and chemical dynamics of mercury species to simulate the broader range of mercury distribution throughout the delineated WOC and EFPC watersheds. A multitude of simulations were completed to calibrate the models, to derive model uncertainties and to provide analysis of remediation scenarios, which have generated gigabytes of simulation data. During FY11 (FIU Year 2), researchers at the Applied Research Center (ARC) at Florida International University (FIU) developed a geodatabase to support the hydrological work being performed at Oak Ridge Reservation (ORR), which serves as a centralized data management system, making the large amounts of data generated from the simulations of contaminant fate and transport accessible to all users. The geodatabase facilitates storage, concurrent editing and import/export of model configuration and output data.

The work for FY12 (FIU Year 3) extended the geodatabase capabilities and created models using ArcGIS ModelBuilder and Python scripting that automate the process of querying the existing EFPC geodatabase and the generation of maps. Investigation of easily downloadable free/open source geographic information systems (GIS) software for viewing and querying the hydrological modeling data and for generating maps, graphs and reports, was then conducted to determine a simple way of sharing project derived data with other project stakeholders such as U.S. Department of Energy (DOE) personnel and ORR site contractors.

The following summarizes the results and conclusions derived from research conducted under this task throughout the FY12 period of performance. Further details are reported in the attached technical report under P3 APPENDIX XII: T4-001: TASK 4 TECHNICAL REPORT.

RESULTS AND DISCUSSION

Work for FY12 has involved the creation of a model using ArcGIS ModelBuilder and Python scripting that automates the process of querying the geodatabase based on specific environmental parameters, performs analyses based on specified algorithms and generates maps with the spatial distribution of computed and observed data. A preliminary literature review was conducted for the use of Python scripting to automate various geoprocessing tasks. Existing and built-in scripts for some of these geoprocesses were also reviewed and in some cases modified to support external query and retrieval of mercury and hydrological model data from the existing ORR geodatabase.

A toolbox which combines built-in ArcGIS geoprocessing tools coupled with customized Python scripts was developed specifically for use with the East Fork Poplar Creek (EFPC) model. These tools and scripts automate the query and retrieval of timeseries data, including contaminant flow and transport parameters (e.g. mercury concentration, surface water and groundwater flow, discharge, groundwater level, etc.), from the existing ORR geodatabase. The ArcGIS data model iterates through selected features and exports the results in tabular format. Existing Python scripts can also be incorporated for statistical analysis of the exported data. Once a feature (e.g. GW well or outfall) has been selected, a field attribute such as station name can be used to extract and export all the data for that station in MS Excel or text format. Geoprocessing such as interpolation of the extracted values and generation of raster images for each day in ESRI GRID and TIFF formats can also be automated. ModelBuilder tools and Python scripts are also available in the toolbox to enable the export of maps from an ArcMap document within a specified data frame in PDF format. In addition, ArcGIS ModelBuilder can be used to generate model workflow diagrams as seen in Figure 25 below, which are a great way of documenting and visually representing the geoprocessing tools and scripts being incorporated into the data model as development progresses.

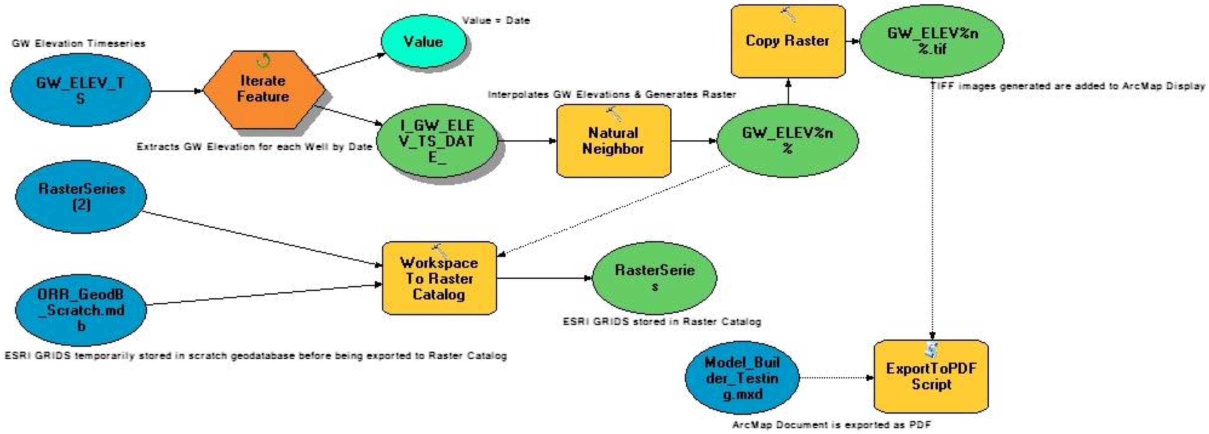

Figure 25. Sample ArcGIS ModelBuilder Process Workflow Diagram.

The GIS tool enables analysis of spatial and temporal monitoring data at ORR. It has been developed as a set of GIS toolboxes that use a set of input GIS files. The tool is calibrated to the project's location (i.e. the EFPC model domain) and is scalable and reusable. The GIS toolbox provides equivalent functionality and has capabilities to:

i. Add GIS files to ArcMap and create layer files.
ii. Select features within a specified area (e.g. the study domain) and zoom to selected features.
iii. Clip/extract selected features and create new layer file of selected subset.
iv. Export clipped feature in format to be used by MIKE SHE/11 model.
v. Export attributes of clipped feature in MS Excel or text format for statistical analysis and generation of graphs and reports.
vi. Export map extent in various formats (e.g. JPEG, TIFF or PDF) for development of reports.
vii. Interpolate timeseries data collected at various monitoring points, generate gridded surfaces, and finally create and export mapped results (as seen in image below).

Representative Python scripts are provided in the Final Technical Report (see P3 APPENDIX XII: T4-001: TASK 4 TECHNICAL REPORT).

A literature and Internet search of easily downloadable free/open source GIS software that can be used for querying the ORR geodatabase online was also carried out in order to facilitate accessibility to the hydrological modeling data as well as the generation of maps, graphs and reports. This way project derived data can be more easily shared with other project stakeholders such as DOE personnel and ORR site contractors. Table 3 below shows the various products reviewed by ARC-FIU.

Table 3. 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/
Google Earth		Windows, Mac OS, Linux	Free	http://www.google.com/earth/index.html

For the purposes of this project, although several products were reviewed, only software that was easy to find on the Internet, readily available, completely free, and simple to download and install were evaluated in depth. Aside from these characteristics, the software products selected also had to be able to perform certain operations and functions such as basic zooming and panning around the map; selection of features and querying of their attributes which contain project derived data stored in the existing ORR geodatabase; addition or removal of georeferenced vector layers and raster imagery to the map; addition of customized symbology and annotation; development, customization, export and printing of map layouts with the option to insert and edit map elements such as a north arrow, scale, legend, map title, etc. Tools for measuring distance and conducting simple buffer analyses were also a consideration. Although at this point of project development very simplistic operations and functions are required, scalable products were given preferential consideration to provide the option of more sophisticated editing and geoprocessing capabilities in the future, particularly with respect to timeseries and hydrological data.

CONCLUSIONS

During FY12, the capabilities of the geodatabase developed by FIU to support the hydrological modeling work being performed for ORR were extended by creating a model using ArcGIS ModelBuilder and Python scripting to automate the process of querying the existing EFPC geodatabase, and to export data that can be used for statistical analysis and the generation of maps, graphs and reports.

With respect to the sharing of project derived data with DOE personnel and ORR site contractors, FIU has suggested that observed and computed timeseries data could be made available through a readily available online mapping interface to facilitate the sharing and dissemination of model output data. Data such as contaminant concentrations and surface/subsurface flow rates can be displayed through development of customized applications which utilize available software APIs. An investigation was conducted to find downloadable software that was easy to find on the Internet, readily available, completely free, and simple to download and install. ArcGIS Explorer Desktop was found to be the most popular and most commonly used free GIS software, however, Quantum GIS was found to be a good competitor and another good option for its extremely user friendly interface, ability to read a broad range of GIS spatial data and text files, feature and attribute editing capabilities, map customization features and the overall quality of the final exported map product. Google Earth also provides a commonly used platform for visualization and analysis of spatial data with built-in base maps and a user friendly interface. Use of the Google Plug-In coupled with an existing “Time” API also facilitates visualization of timeseries data. MapWindow GIS and Tatuk GIS were also two useful data viewers, but had less functionality than ArcGIS Explorer Desktop and Quantum GIS. HydroDesktop, although limited for the same reasons as MapWindow GIS which it is based upon, is also a good consideration if users want to ability to access, visualize and analyze hydrologic and climate data, which may prove useful given the nature of the hydrological modeling work that this project is based upon. GRASS GIS, although extremely sophisticated in its level of functionality especially for a free product, was not as straightforward to set up as some of the other free/open source viewers reviewed and may have the potential to consume valuable time which can deter some end users. ArcReader and DIVA-GIS both lacked the level of desired functionality and were therefore omitted from further consideration.

During a project review televideoconference between FIU and DOE held 04/30/13, DOE-HQ expressed interest regarding the security aspect of sharing the geodatabase with emphasis placed on the fact that the integrity of the data would need to be maintained and the cyber issues understood in addition to the software issues. Sharing via the web requires proper implementation of security protocols in terms of sharing the geodatabase and ensuring integrity of the data. FIU clarified that in addition to the FIU-ARC firewalls and the built-in software and hardware security protocols, all computers must adhere to the FIU's University Technology Services (UTS) Security and IT Policies which are outlined in detail at http://it.fiu.edu/security/index.shtml. Security measures such as password protection can also be implemented. FIU also added that they would work with DOE to develop a security strategy for sharing the database within DOE or, if the issue arose, with an outside party if necessary.

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TASK 5: STUDENT SUPPORT FOR MODELING OF GROUNDWATER FLOW AND TRANSPORT AT MOAB SITE, UTAH

INTRODUCTION

FIU, in collaboration with DOE's Moab site project director, has utilized an existing groundwater numerical model to evaluate the tailings pore-water seepage in order to assist in effective dewatering of the tailings pile and to optimize the groundwater extraction well field as part of the DOE Uranium Mill Tailings Remedial Action (UMTRA) for the Moab site. The work was carried out with support from student interns who assisted in the collection of groundwater samples and site data and applied the existing groundwater and transport model (SEAWAT available from the public domain) to analyze the groundwater flow and transport data of the Moab site.

The objective of this model is to analyze the nitrogen and uranium cycle in the environment and provide forecasting capabilities for the fate and transport of contamination within the Moab site and to provide information which can be used to determine the efficiency of remedial actions in reducing the concentration and load of contaminants and to assist DOE in deciding the effectiveness of remedial actions. Modeling was performed with MODFLOW, SEAWAT and FEFLOW as a benchmark. The main objective was to determine the effect of discharge of a legacy ammonia plume from the brine zone after the extraction wells and injection system have been shut off. The model was used to predict capture zones for different operating scenarios, mass removal, and time to complete remediation.

The following summarizes the results and conclusions derived from research conducted under this task throughout the FY12 period of performance. Further details are reported in the attached technical report under P3 APPENDIX XIII: T5-001: TASK 5 TECHNICAL REPORT.

RESULTS AND DISCUSSION

The existing Moab model was revised and updated with additional information related to the current remedial actions which include injection, well withdrawal, and simulating the fate and transport of contaminants, including uranium and ammonia, in the subsurface domain at the Moab site in Utah and how density dependent flow is related to brines in the groundwater system beneath the site. Information such as ammonia surface water data collected between 2000 and 2002 were used in the analysis.

The model was also updated by implementing geostatistically interpolated ammonia and uranium plumes and current well operation data into the model to evaluate the effects of pumping on contaminant concentrations and determining potential surface water concentrations in riparian habitat areas for a range of operating conditions. The plumes of aqueous species of concern (nitrate, uranium) were developed with the width of the tailings that would be conservative.

After implementing plumes into the model as initial conditions, additional simulations were conducted to optimize mass removal and capture from the existing system. The ammonia transport was simulated by applying as an initial condition the ammonia plume (for a couple of cycles), and determining the yearly rise and fall in the river to determine if the ammonia concentrations moving up into the brine zone is due to the fluctuations of concentrations in the river.

The effects of the brine zone beneath the site on an overlying saline zone and the effect of discharge of a legacy ammonia plume from the brine zone after the extraction wells and injection system have been shut off and the spatial extent of the discharge zone for the ammonia legacy plume in the brine zone and its effect on natural flushing were determined.

A diversion ditch was added to intercept and extract water from the tailings. The ditch was implemented into the flow model (as drain cells) and by setting the head, levels will be set in each drain cell at the elevations of the drains. A new configuration was implemented that includes infiltration and provides information about the reoccurrence of the concentrations within the recharge assuming the existence of a freshwater lens. The effect of mixing water from the river and the diversion ditch was determined along with the benefits of running a diversion ditch and well extraction at the same time

The hydrologic parameters of the tailings were analyzed and a series of simulations were used to provide information which showed that prescribed-head variable upper boundary condition in eliminated the errors resulting from quantifying net infiltration and evaporation through the filter layer of the cover. Model results indicate a long term uniformly unsaturated hydraulic barrier with a low unsaturated hydraulic conductivity and a low flux under a gradient of unity and that after a few decades the tailings may transmit minimal amounts of seepage to the groundwater system.

The gravimetric moisture contents of more than 70 tailing samples at Moab for modeling were also analyzed. The volume of the sample and specific gravity of the sample were analyzed to determine the percent saturation. From the analysis it was determined that the % moisture ranges from 6.5% to 92.9%, with an average of 38.5%. The fine sand samples had the lowest values (from 6.5 to 8.4%). The data was introduced into the hydrological model and a set of simulations were performed to determine the difference with the previous simulations. This provided additional information about the uncertainty of the hydrological parameters. The hydrological model also provided calculation about the distribution of moisture content in the soil column as a function of precipitation.

The numerical model was modified to provide capabilities for analysis of the fluctuation of moisture content which was determined on a daily basis at different soil column heights. The purpose was to provide information about the exchange of flux between the unsaturated and saturated zones and therefore gain a better understanding of the vertical contaminant fluxes from the mine tailings to the subsurface flow, and subsequent horizontal transport to the river. Additional simulations were conducted to determine the transient drainage of moisture in the tailings by quantifying the vertical downward fluxes which are a result of drainage of the mine tailings. The model simulations were used to determine the fraction of precipitation infiltrating the tailings, the extent of infiltration, and the fraction of surface runoff during precipitation events. A series of probability exceedance figures were developed for each selected tailings layer to provide understanding of the behavior of the tailings during wet, median and dry conditions.

A paper based on this research was presented at the Waste Management Symposium (WM 2013) in February 2013 entitled “Long-Term Performance of Uranium Tailings Disposal Cells” by

Georgio Tachiev, Kent Bostic, Anamary Daniel, Ken Pill, Viviana Villamizar and Nantaporn Noosai. The presentation focused on results of simulations that were used to understand the dynamics of the system and changes in moisture and moisture flux. The following results were derived:

- The analysis considered the stochastic variation of all hydrological events that control flow and transport at the site. A unique modeling approach simulated the daily climatic conditions and determined the changes in moisture and moisture flux from the disposal cell for a period of ten years.
- Modeling results indicated that increases in the saturated conductivity at the top of radon barrier do not influence flux from the tailings with time because the tailings behave similar hydraulically to the radon barrier.
- The presence of a thin layer of low conductivity material anywhere in the cover or tailings restricts flux in the worst case to the saturated conductivity of that material. Furthermore, the precipitation is equivalent to the evapotranspiration losses from the surface layer.
- Where materials are unsaturated at depth within the radon barrier of tailings slimes, conductivities are typically less than 10-8 centimeters per second.
- If the low conductivity layer is deep within the disposal cell, its saturated properties are less likely to change with time.

CONCLUSIONS

To understand the dynamics of the system and changes in moisture and moisture flux it is important to consider the stochastic variation of all hydrological events that control flow and transport at the site. A unique modeling approach simulated the daily climatic conditions and determined the changes in moisture and moisture flux from the disposal cell for a period of ten years. Modeling results indicated that increases in the saturated conductivity at the top of radon barrier do not influence flux from the tailings with time because the tailings behave similar hydraulically to the radon barrier. The presence of a thin layer of low conductivity material anywhere in the cover or tailings restricts flux in the worst case to the saturated conductivity of that material. Furthermore, the precipitation is equivalent to the evapotranspiration losses from the surface layer. Where materials are unsaturated at depth within the radon barrier of tailings slimes, conductivities are typically less than 10-8 centimeters per second. If the low conductivity layer is deep within the disposal cell, its saturated properties are less likely to change with time.

The model confirmed the following trends:

a) **Infiltration and evapotranspiration:** The accumulated infiltration is equivalent to the accumulated evapotranspiration, resulting in no water reaching the groundwater tailings under the conditions simulated (daily precipitation and evapotranspiration). In general, for the hydrologic conditions at the site, the water from precipitation infiltrates in the shallow surface zone, where it is lost from evapotranspiration.

b) **Extent of Infiltration:** At a depth of 0.7 ft in the rip-rap layer (1st layer) the moisture content is very low, implying that there is a low possibility of water reaching past that layer (hydraulic conductivity is in the order of 10-10 m/s).

c) **Vegetation:** The vegetation affects the rate of evapotranspiration, increasing the amount of evaporation thus reducing the amount of water that infiltrates through the layer.

d) **Land cover:** The rip-rap rock cover variations in hydraulic conductivity ranges from 10^{-6} to 10^{-4}. There is no concern that rock rip-rap is increasing percent saturations and downward moisture flux.

The significance of this modeling approach is that the stochastic variations of a variety of hydrologic events are taken under consideration and provide a better understanding of the flow and transport within the site. Therefore, both the operation and the maintenance of the disposal cells can be minimized if they are allowed to progress to a natural condition with some vegetation and soil genesis. Because the covers and underlying tailings have a very low saturated hydraulic conductivity after transient drainage, eventually the amount of moisture leaving the tailings has a negligible effect on groundwater quality. Although some of the UMTRA sites are not in compliance with the groundwater standards, the explanation may be legacy contamination from mining, or earlier higher fluxes from the tailings or unlined processing ponds. Investigation of other legacy sources at the UMTRA sites may help explain persistent groundwater contamination.

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FUTURE WORK

For FY2013, FIU is proposing a scope which builds upon previously developed models to analyze flow, fate and transport of site contamination and remedial activities at the OR and Moab sites. This work is synergistic with the work ORNL is performing and will involve the integrated surface/subsurface flow and transport model developed for the EFPC, the surface model developed to study the drainage discharges from the outfalls along EFPC, and the variable density model for the Moab site. A series of simulations, coordinated with the site, will be developed to provide better understanding of the mercury dynamics within the OR watersheds (i.e., EFPC, Y-12 NSC, Bear Creek, and WOC) for variable environmental conditions and for specified remediation alternatives. In addition, the XPSWMM modeling work conducted for White Oak Creek will be conducted on the premise that this smaller system could be modeled at ORNL to prove the concept and then expanded to a larger area at Y-12. However, security issues at Y-12 will need to be addressed. Student support will also be provided for numerical modeling of subsurface flow and transport of the Moab Uranium Mill Tailings Remedial Action (UMTRA) site. Stochastic analysis will be performed on measured and computed hydrological and transport data, including flow and pollutant concentrations at each outfall. The overarching geodatabase at FIU will be updated with recent monitoring and simulation data to provide remote access, storage and retrieval of the data for analytical and reporting purposes.

FIU proposes to add new scope in FY2013, focused on EM pilot studies and software use to evaluate the benefit of sustainable remediation practices; quantify the environmental footprint of remedial and other alternatives; and develop a sustainable optimization module for monitoring program analysis on EM sites. Sustainability evaluation, integrated into existing 5-year regulatory reviews is a common industry and federal practice to assess footprint impact, as well as to improve system design performance and efficiency.

Task 3.1: EFPC Model Update, Calibration, and Uncertainty Analysis

The objective of this task is to provide analysis of the coupling between hydrology and mercury transport within the context of decreasing the risk of decontamination and decommissioning (D&D) activities. The major deliverable is numerical and stochastic analysis of observed and computed timeseries for flow and contaminant concentration for National Pollutant Discharge Elimination System (NPDES)-regulated outfalls within the watershed. To solve the challenges related to analysis of contaminants within the EFPC domain, FIU has developed a numerical model of the entire EFPC watershed. The model was used to determine the impact of remediation alternatives on the complete hydrologic cycle, the transport overland and in surface water and rivers, sediment transport and reactions, and mercury exchange with sediments. The model simulations accounted for a range of hydrological impacts related to planned remediation alternatives. The work proposed for 2013 will support a PhD student and will include using the model to provide simulations that implement selected main thermodynamic equilibria and reactions. The proposed scope under this task for FY13 will have a 20% allocation.

> **Subtask 3.1.1:** Review the existing Hg thermodynamic database and provide an update for the EFPC environmental conditions. The dissolution mechanism of the mercury beads within the EFPC watersheds which will be reviewed and the competitive absorption on the

EFPC sediment between the major cations contained in EFPC water (Ca^{2+}, Mg^{2+}, etc.) and Hg^{2+} will be investigated. The deliverable from this task will include the Hg thermodynamic database relevant to EFPC environmental conditions that will be further utilized for and integrate into the integrated flow and transport models already developed for the site (PHREEQC, XPSWMM, MIKE).

Subtask 3.1.2: The task will provide integration of the Hg thermodynamic database into the existing EFPC model. The integrated model will have improved capability to simulate the exchange of Hg between the creek and river, the distribution of mercury species within pore water, sorbed mercury within pores, sorbed mercury on suspended particles and "free" mercury (dissolved and chelated mercury species). The deliverables from this task will include the analysis of different remediation scenarios including hydrological and geochemical methods, tools that can be utilized to investigate the best remediation methods to address these issues.

Subtask 3.1.3: Provide a series of simulations using the EFPC model and the thermodynamic and kinetic interactions. For these simulations, provide statistical analysis of observed data and development of timeseries, probability exceedance curves, and probability distribution models of flow, concentration and load data that integrate already downloaded data and new data as it becomes available. The data will include groundwater well monitoring, concentrations in groundwater wells, outfall flow, and concentration and load data. The deliverable of this subtask will include timeseries, probability exceedance curves, load exceedance curves, probability distribution models for each monitoring point and a report. The subtask will provide improved estimates for the stochastic nature of mercury fluxes within the EFPC domain.

Task 3.2: Simulation of NPDES and TMDL Regulated Discharges from Non-Point Sources for EFPC and Y-12 NSC.

This task will develop a surface flow model for Y-12 NSC similar to the model developed for ORNL. The purpose of the model will be to determine the discharges from the stormwater drainage system and for each of the outfalls along EFPC. Subsequently the discharges will be implemented in the surface and groundwater model which was developed for the entire EFPC. A series of simulations will provide numerical analysis of contaminant flow and transport within the EFPC watershed and will determine the impact of model parameters on NPDES and TMDL regulations. The task will support an MS student. The proposed scope under this task for FY13 will have a 10% allocation.

Subtask 3.2.1: Re-creation of the existing Y-12 NSC stormwater management system layout via a numerical surface water one dimensional XPSWMM model to provide a better understanding of the flow patterns on-site, including flow rates as a function of rainfall intensity and the fraction of drainage volumes and rates reaching each outfall. The deliverable of this subtask will be a calibrated and validated drainage model that will provide detailed analysis of how much water reaches each outfall and the source of the water. By providing better understanding of the drainage system, the site will be provided with a tool that can be used to investigate the best remediation scenarios for setting up remediation priorities, e.g., helping identify the greatest contributors to mercury loads.

Subtask 3.2.2: Use of the discharges determined in Subtask 2.1 to provide simulations of the entire EFPC watershed and the load discharge at Station 17. The deliverable of this subtask will include development of probability exceedance curves for each scenario; this data will provide additional insight of the effect for the entire range of hydrologic regimes (very wet to very dry conditions). The task will study the modifications of the hydrology which limit the amount of overland flow over site surfaces, and limit the infiltration of rainwater through areas with underlying mercury contamination.

Task 3.3: Sustainable Remediation and Optimization: Cost Savings, Footprint Reductions, and Sustainability Benchmarked at EM Sites

This is a new task to be incorporated into the Project 3 work scope for FY13 (FIU Year 4). DOE's Offices of EM and Health, Safety, and Security (HSS) established a cross-programmatic team in 2012 to benchmark, train, and evaluate the cost-benefit of Green & Sustainable Remediation (GSR) practices applied to cleanup and closure projects at the field sites and Headquarters' management of those projects. EM worked with EPA and the Interstate Technology & Regulatory Council (ITRC) to certify over 130+ DOE staff and cleanup contractors in GSR principles and practice training. Federal agencies and industry are primarily using the public domain SITEWISE™ software [developed and sponsored by Battelle, the Navy, and the US Army Corps of Engineers (USACE)] to improve sustainability of remedial and monitoring decisions; identify improved and more cost-effective end states; and to reduce hazardous emissions, consumption of water and energy resources, as well as footprint impact. The benefits of implementing two new ASTM standard guidance for GSR are expected to be transformative to the remediation industry, by greatly lowering costs and improving effectiveness of remediation strategies applicable to soil, groundwater, radioactive waste, and facility D&D.

The SITEWISE™ software is an EXCEL-based evaluation tool designed to: 1) compare and contrast alternatives for remedial, monitoring, waste handling, and D&D design, and 2) to generate results for cost benefit and sustainable decision-making for regulatory compliance. The Navy, EPA, and USACE incorporate sustainability evaluation and decision making into their long-standing and successful optimization programs as part of the 5-year regulatory review process. SITEWISE™ is one of many evaluation tools used in federal and industry sectors to calculate and optimize the environmental footprint of cleanup and closure alternatives. Specifically, SITEWISE™ methodology provides a baseline assessment of long-term alternative design impacts based on the sustainability factors of greenhouse gas (GHG) and critical air pollutant (i.e., sulfur and nitrogen oxides, particulate matter, etc.) emissions; energy and water usage; natural resource consumption and footprint impact; waste generation; and risk from accident death and injury.

A sustainability assessment is typically carried out using a building block approach where every alternative is first broken down into modules that mimic the implementation phases. For a remedial action, sustainability factors are calculated for the investigation, construction, operation, and long term monitoring phases to estimate the overall footprint of the remedial alternative. This building block approach reduces redundancy in the sustainability evaluation and facilitates the identification of specific activities that have the greatest environmental footprint. The objective of the methodology is to provide a decision matrix for remedy selection, design, or implementation. This approach allows for a remedy optimization stage as well. The methodology is a standard requirement for remediation and optimization led at sites by the EPA, Navy, Army, Air Force, and USACE. The proposed scope under this task for FY13 will have a 50% allocation.

Subtask 3.3.1: Benchmarking of current methodology using SITEWISE™. The 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. These pilot studies will also provide valuable insight regarding how EM cleanup and closure contracts can be modified, incentivized, and improved to attain sustainable goals and optimize existing designs. FIU will work with EM HQ and interested field sites to obtain the necessary field data to conduct pilot-scale sustainability evaluations using SITEWISE™. FIU engagement with sites and HQ to identify "pilot-scale sustainability evaluations" should also include all EM's principle problem areas – High-Level Waste, Soil & Groundwater, Transuranic Waste, Deactivation & Decommissioning (and others as identified). Further, it must be FULLY coordinated with EM's Facility Engineering Program.

Subtask 3.3.2: Implementation of a SITEWISE™ module for sustainable analysis and optimization of monitoring programs. This subtask will focus on the design and development of a module in SITEWISE™ for the user to evaluate sustainable approaches, technologies, and optimization of site monitoring networks and variables. SITEWISE™ can be improved to include a monitoring design and optimization module, whereby users are guided through an expert system to select sustainable technologies and practices to reduce monitoring project costs, efforts, and footprint impact. Then, SITEWISE™ will be programmed to lead the user through data input and analytical options to generate sustainable results and lifecycle cost savings for various designs. A SITEWISE™ monitoring module will be evaluated to receive data and export results though a geographic information system (GIS) interface to take full advantage of temporal and spatial analyses and visualizations offered by a GIS platform. For example, if a statistical or geostatistical software, such as MAROS or GTS, is used to downsize a compliance monitoring program (i.e., remove wells, analytes, or frequencies), the monitoring module in SITEWISE™ will accept these results via GIS or EXCEL to calculate the reduction in emissions, energy and water usage, waste generation, and accident risk over the program total life cycle. FIU will work with EM to create a monitoring program module with a sustainability expert system and GIS interface to improve data import, analysis, and visualization. It is likely that a monitoring program module in SITEWISE™ is of equal value and interest to other federal agencies and the private sector. It could be co-developed with leveraged funding from other federal partners such as EPA, Navy, and USACE. GIS programming tools will be developed and integrated within the modules to provide capability for processing using standard spatial database and applications (such as ArcMap).

Subtask 3.3.3: Calibration and Verification of the SITEWISE™ monitoring program module. FIU will collaborate with other federal agency experts and their contractors to assure benchmark studies for calibration and verification of this module.

Task 3.4: Geodatabase Development for Hydrological Modeling Support

During FY11-FY12, FIU developed a geodatabase to support the hydrological modeling work being performed at OR which serves as a centralized data management system, providing access to data generated from simulations of contaminant fate and transport to all users and facilitating storage, concurrent editing and import/export of hydrological model data. The capabilities of the geodatabase were then extended by creating a model using ArcGIS ModelBuilder and Python scripting to automate the process of querying the existing EFPC geodatabase, and to export data that can be used for statistical analysis and the generation of maps, graphs and reports. The geodatabase which has been developed at FIU is focused on storage and retrieval of hydrological data which is used in the hydrological and transport models. In addition, the database stores files that are specific to the DHI Software and hydrologic models being used. An investigation of downloadable freeware to facilitate online querying of the database was also conducted to determine methods by which project derived data can be more easily shared with other project stakeholders such as DOE personnel and ORR site contractors. The proposed scope under this task for FY13 will have a 10% allocation.

The proposed scope for **FY13** involves the following subtasks:

Subtask 3.4.1: Update existing EFPC geodatabase with more recent OR site monitoring data available from various sources including OREIS, USGS, NRCS STATSGO or SSURGO soil databases, and the U.S. EPA MRLC or NALC land cover databases. Training will also be provided to FIU graduate and/or undergraduate students on how to update and query the existing geodatabase within the ArcGIS environment.

Subtask 3.4.2: Work on development of customized Python scripts which will serve to enhance database querying capabilities. FIU will implement a library of scripts which can be coupled with other existing libraries used for mathematics, science, and engineering such as NumPy and SciPy, to perform statistical analyses and which can be applied to similar databases used at other DOE sites. ArcGIS ModelBuilder will be used to document ArcGIS model workflow diagrams for reporting purposes.

Subtask 3.4.3: Use the existing geodatabase structure developed for the EFPC modeling work at OR to create similar databases to support modeling work being conducted at the Moab Site, Utah, and other EM cleanup sites that may be included in Task 3.3 as pilot studies.

Task 3.5: Student Support for Modeling of Groundwater Flow and Transport at the Moab Site, Utah

FIU, in collaboration with the DOE's Moab site, is using an existing groundwater numerical model to evaluate the tailings pore-water seepage in order to assist in effective dewatering of the tailings pile and to optimize the groundwater extraction well field as part of the DOE UMTRA for the Moab site. The work was carried out with support from student interns who assisted in the collection of groundwater samples and site data and applied the existing groundwater and transport model (SEAWAT available from the public domain) to analyze the groundwater flow and transport data of the Moab site. The objective of this model is to analyze the nitrogen and uranium cycle in the environment and provide forecasting capabilities for the fate and transport of contamination within the Moab site and to provide information which can be used to determine the efficiency of remedial actions in reducing the concentration and load of contaminants and to assist DOE in deciding the effectiveness of remedial actions. Modeling is to be performed with SEAWAT (and FEFLOW for benchmarking and to determine the interactions between the River and the subsurface zone). The current model was set up to simulate only 13 periods (total of 13 months) using average monthly boundary conditions. This was a model limitation which does not provide sufficient information to determine the flow and transport, and most importantly the impact of daily extreme events for critical time periods that can impact the habitats along Colorado River. During FIU Year 4, a PhD student will work with the existing transport model to complete this task's work scope by performing numerical simulations of remedial scenarios and developing a PhD dissertation.

The main objective will remain determining the effect of discharge of a legacy ammonia plume from the brine zone during operation of extraction wells and injection system, and after they have been shut off using daily simulation timesteps. The model will be used to predict capture zones for different operating scenarios, mass removal, and time to complete remediation. The proposed scope under this task for FY13 will have a 10% allocation.

The proposed scope for **FY13** involves the following subtasks:

Subtask 3.5.1: Update the existing model using daily timesteps instead of monthly average values of the boundary conditions. Provide an update to the existing Moab model by implementing daily timeseries which will more accurately represent the hydrologic cycle. The current model uses monthly timeperiods which are based on average monthly hydrologic data. This underestimates possible daily fluctuations, including rainfall, river stages. Currently, data are available for groundwater levels, water stages, rainfall and evapotranspiration.

Subtask 3.5.2: Conduct simulation scenarios using daily timesteps. Conduct simulations with the SEAWAT model using daily timesteps to analyze daily variations of the nitrogen and uranium cycle in the environment, determine the exchange with the Colorado River and provide forecasting capabilities for the fate and transport of contamination within the Moab site for daily timesteps.

APPENDICES

The following documents are available at the DOE Research website for the Cooperative Agreement between the U.S. Department of Energy Office of Environmental Management and the Applied Research Center at Florida International University: http://doeresearch.fiu.edu

1. P3 APPENDIX I FY12 Project Technical Plan
2. P3 APPENDIX II Project Overview Presentations
3. P3 APPENDIX III Progress Report - XPSWMM Model Preliminary Configuration Parameters
4. P3 APPENDIX IV Progress Report - XPSWMM Model Preliminary Results Summary
5. P3 APPENDIX V Progress Report - Preliminary Results Summary of Laboratory Experiments
6. P3 APPENDIX VI Progress Report - Sample Python Scripts and Model Builder Process Workflow Diagrams
7. P3 APPENDIX VII Progress Report - Preliminary Results Summary for the Moab Model
8. P3 APPENDIX VIII Publications
9. P3 APPENDIX IX Conference Proceedings
10. P3 APPENDIX X: T1T2-001 Tasks 1-2 Technical Report
11. P3 APPENDIX XI: T3-001 Task 3 Technical Report
12. P3 APPENDIX XII: T4-001 Task 4 Technical Report
13. P3 APPENDIX XIII: T5-001 Task 5 Technical Report