Recent Approaches to Modeling Transport of Mercury in Surface Water and Groundwater - Case Study in Upper East Fork Poplar Creek, Oak Ridge, TN – 13349

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ABSTRACT

In this case study, groundwater/surface water modeling was used to determine efficacy of stabilization in place with hydrologic isolation for remediation of mercury contaminated areas in the Upper East Fork Poplar Creek (UEFPC) Watershed in Oak Ridge, TN. The modeling simulates the potential for mercury in soil to contaminate groundwater above industrial use risk standards and to contribute to surface water contamination. The modeling approach is unique in that it couples watershed hydrology with the total mercury transport and provides a tool for analysis of changes in mercury load related to daily precipitation, evaporation, and runoff from storms. The model also allows for simulation of colloidal transport of total mercury in surface water. Previous models for the watershed only simulated average yearly conditions and dissolved concentrations that are not sufficient for predicting mercury flux under variable flow conditions that control colloidal transport of mercury in the watershed. The transport of mercury from groundwater to surface water from mercury sources identified from information in the Oak Ridge Environmental Information System was simulated using a watershed scale model calibrated to match observed daily creek flow, total suspended solids and mercury fluxes. Mercury sources at the former Building 81-10 area, where mercury was previously retorted, were modeled using a telescopic refined mesh with boundary conditions extracted from the watershed model. Modeling on a watershed scale indicated that only source excavation for soils/sediment in the vicinity of UEFPC had any effect on mercury flux in surface water. The simulations showed that colloidal transport contributed 85 percent of the total mercury flux leaving the UEFPC watershed under high flow conditions. Simulation of dissolved mercury transport from liquid elemental mercury and adsorbed sources in soil at former Building 81-10 indicated that dissolved concentrations are orders of magnitude below a target industrial groundwater concentration beneath the source and would not influence concentrations in surface water at Station 17. This analysis addressed only shallow concentrations in soil and the shallow groundwater flow path in soil and unconsolidated sediments to UEFPC. Other mercury sources may occur in bedrock and transport though bedrock to UEFPC may contribute to the mercury flux at Station 17. Generally mercury in the source areas adjacent to the stream and in sediment that is eroding can contribute to the flux of mercury in surface water. Because colloidally adsorbed mercury can be transported in surface water, actions that trap colloids and or hydrologically isolate surface water runoff from source areas would reduce the flux of mercury in surface water. Mercury in soil is highly adsorbed and transport in the groundwater system is very limited under porous media conditions.

INTRODUCTION

In this case study, groundwater/surface water modeling was used to determine efficacy of stabilization in place with hydrologic isolation for remediation of mercury contaminated areas in the Upper East Fork Poplar Creek (UEFPC) Watershed in Oak Ridge, TN. The modeling simulates the potential for mercury in soil to contaminate groundwater above industrial use risk standards and to contribute to surface water contamination. The modeling approach is unique in that it couples watershed hydrology with the total mercury transport and provides a tool for analysis of changes in mercury load related to daily precipitation, evaporation, and runoff from storms. The model also allows for simulation of colloidal transport of total mercury in surface water. Previous models for the watershed only simulated average yearly conditions and dissolved concentrations that are not sufficient for predicting mercury flux under variable flow conditions that control colloidal transport of mercury in the watershed. The transport of mercury from groundwater to surface water from mercury sources identified from information in the Oak Ridge Environmental Information System was simulated using a watershed scale model calibrated to match observed daily creek flow, total suspended solids and mercury fluxes. Mercury sources at the former Building 81-10 area, where mercury was previously retorted, were modeled using a telescopic refined mesh with boundary conditions extracted from the watershed model. The modeling simulated the potential for mercury in soil to contaminate groundwater above industrial use risk standards and to contribute to surface water contamination at a surface water integration point (Station 17) downstream in UEFPC (Fig. 1).

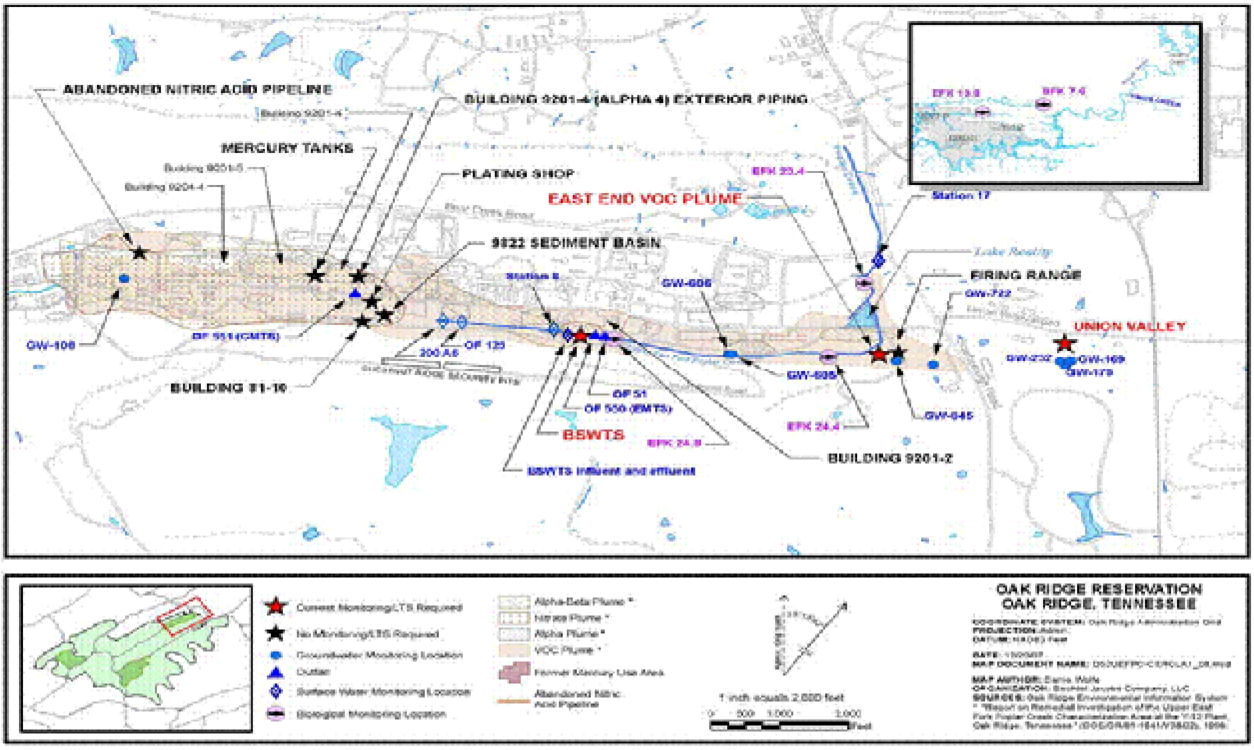


Fig. 1. Locations of Outfalls at UEFPC (3)

The modeling was used to assess whether Remedial Actions would meet an interim surface water goal in the UEFPC Phase II ROD of 200 parts per trillion (ppt) [1] and possibly an instream recreational Ambient Water Quality Criteria of 51 ppt at Station 17 in UEFPC (Fig. 2) or an Industrial Groundwater Use Risk Standard of 0.036 milligrams per liter (mg/L) [2].

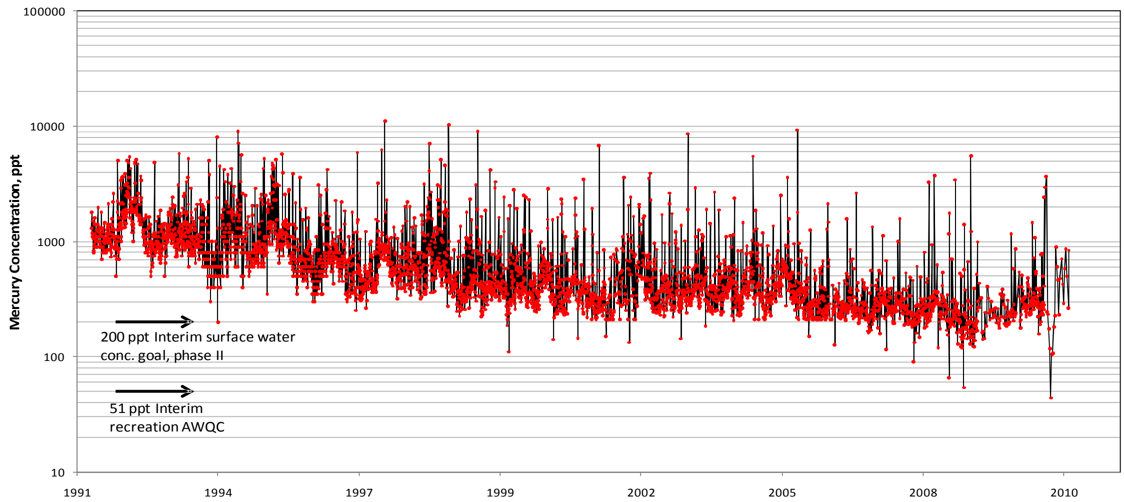


Fig. 2. Mercury Concentrations in UEFPC at Station 17 Relative to Interim Goals

SITE DESCRIPTION

Mercury was used at production facilities in the watershed from the 1950s and presents ecologic risk due to bioconcentration of methyl mercury in fish. Between 1953 and 1983, it is estimated that 109,000 kilograms (kg) of mercury were released during the operation of the separation processes at the Y-12 Plant. Although the release of high concentrations of mercury from the plant stopped in 1963, mercury continues to be released from various point and nonpoint sources of contamination.

Dry weather loading of mercury to the UEFPC has multiple sources, including infiltration of contaminated shallow groundwater into the storm water drain network, dissolution of mercury from the contaminated pipes, advection of contaminated sediment water into the surface flow, and emergence of contaminated groundwater from the karst system in springs and seeps [3]. A new site conceptual model indicated that much of the mercury discharged into UEFPC is from storm drain Outfall 200 in the West End Mercury Area with additional sources from sediment in the steam bed and groundwater discharge (Fig. 3). A major source is treated by the Big Spring Treatment System that removes high concentrations of mercury from Outfall 51 [3]. Liquid elemental mercury and high concentrations were found in soil near the former Building 81-10 area, where mercury was retorted in a roaster (Fig. 4) [4]. There was concern whether this mercury could be creating a plume above an industrial risk groundwater level in shallow groundwater in unconsolidated sediments, enter UEFPC, and affect surface water at Station 17.

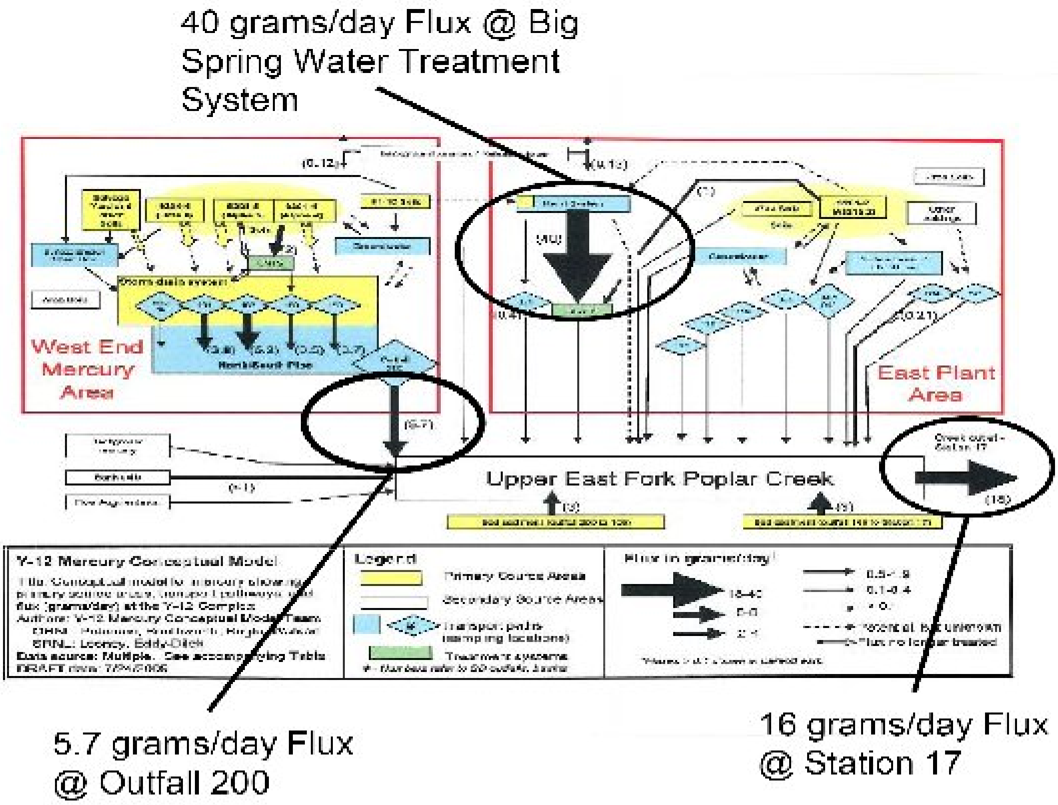


Fig. 3. Site Conceptual Flux Model of Discharges to UEFPC [3]

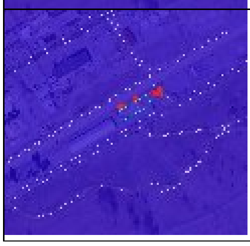
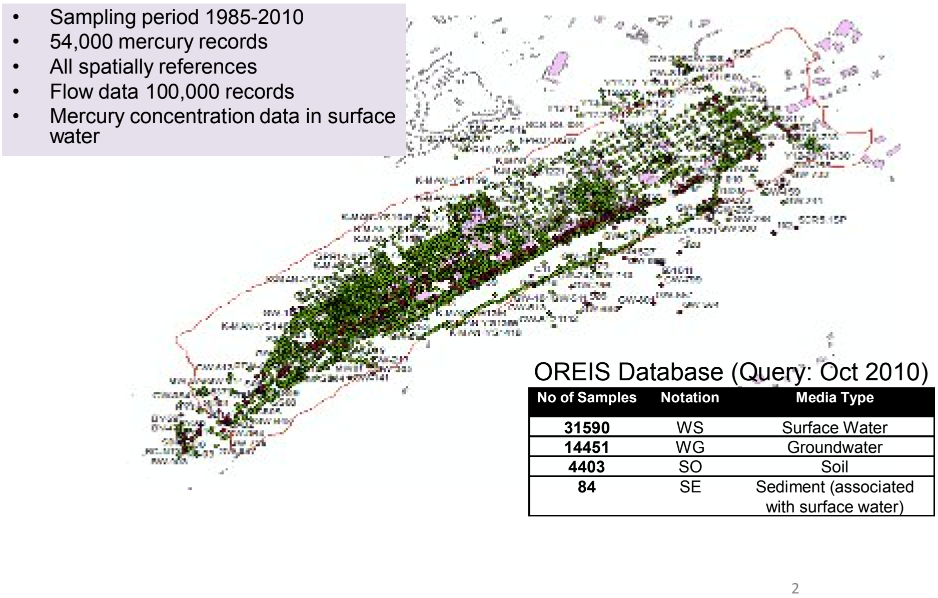
Sources in Soil	Method of Detection	Depth	Model Input
	High Concentration Adsorbed Mercury (from laboratory analysis of total mercury in soil samples).	Occurs are variable depths from 0 to 2 meters in the unsaturated zone.	The model implements the contaminated area as a sorbed source with initial concentration of 325 milligrams/kilogram (mg/kg) average concentration.
	Liquid Elemental Mercury (from visual observation of core samples).	Depth of 1 to 8 meters (average depth of 4 meters used)	The model implements the contaminated area as a continuous source, Hg = 60 ppb (equivalent to solubility limit). Source was implemented in the unsaturated and saturated zones.
	X Ray Flourescent Measurements of mercury exceeding 200 parts per milliom (ppm)	Depth of 0 to 8 meters (according to the location)	The model implements the contaminated area as a sorbed source with initial concentration of 200 mg/kg average concentration Source is implemented in the unsaturated zone, and in the saturated zone as 200 ppm

Fig. 4. Mercury Sources in the Vicinity of Former Building 81-10

MODELING APPROACH

A transport model was constructed and calibrated from historical mercury sample results and flow records obtained from OREIS in the model domain Fig. 5. The model domain was bounded by ridges to the north and south and groundwater and surface water divides in the watershed. The model includes 57 outfalls along UEFPC which have been listed in the National Pollutant Discharge Elimination System permit (Fig. 1).



No of Samples	Notation	Media Type
31590	WS	Surface Water
14451	WG	Groundwater
4403	SO	Soil
84	SE	Sediment (associated with surface water)

Fig. 5. Recent Mapping of Mercury in the Watershed Model Domain

Ground and surface water hydrodynamics as well as advection/dispersion calculations were performed with MIKESHE and MIKE11 models, while the interactions between mercury, sediment, and water were simulated using ECOLAB (Fig. 6). The watershed model was calibrated to match observed daily creek flow, total suspended solids, and mercury flux (load) (Fig. 7). To model mercury source areas at the former Building 81-10 area, a telescopically refined mesh was used to create a submodel with boundary conditions extracted from the watershed model (Fig. 8). Model input coverages also were extracted from the watershed model and input into the submodel (Fig. 9). Subsurface hydrology including flow in the unsaturated zone, a variable water table, and hydraulic conductivity zones and their relation to geology are shown on Fig. 10. Model calibration compared observed and predicted heads for daily time steps using daily precipitation and evaporation input (Fig. 11). Model predicted groundwater velocity vectors indicated a convergence of flow towards the center of the watershed and then flow down the valley towards UEFPC (Fig. 12).

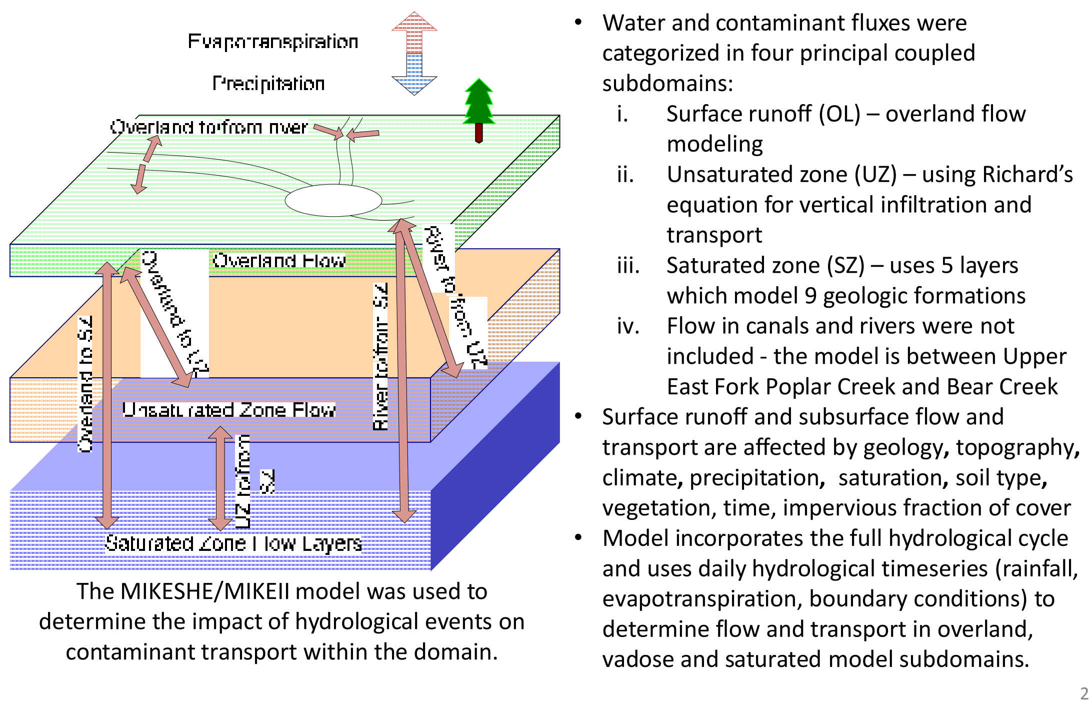


Fig. 6. Technical Basis for Contaminant Fate and Transport in Watershed Scale Model

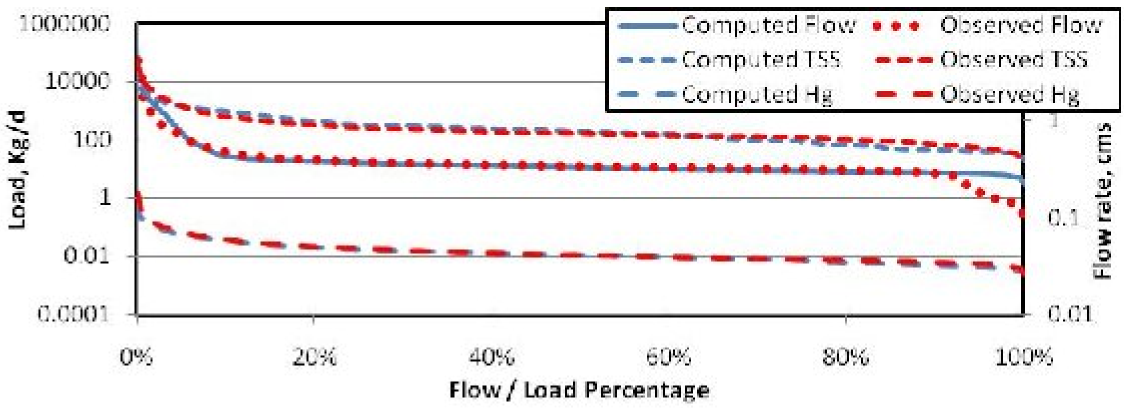


Fig. 7. Computed VS Observed Flow, TSS, and Hg Load Duration Curves at Station 17

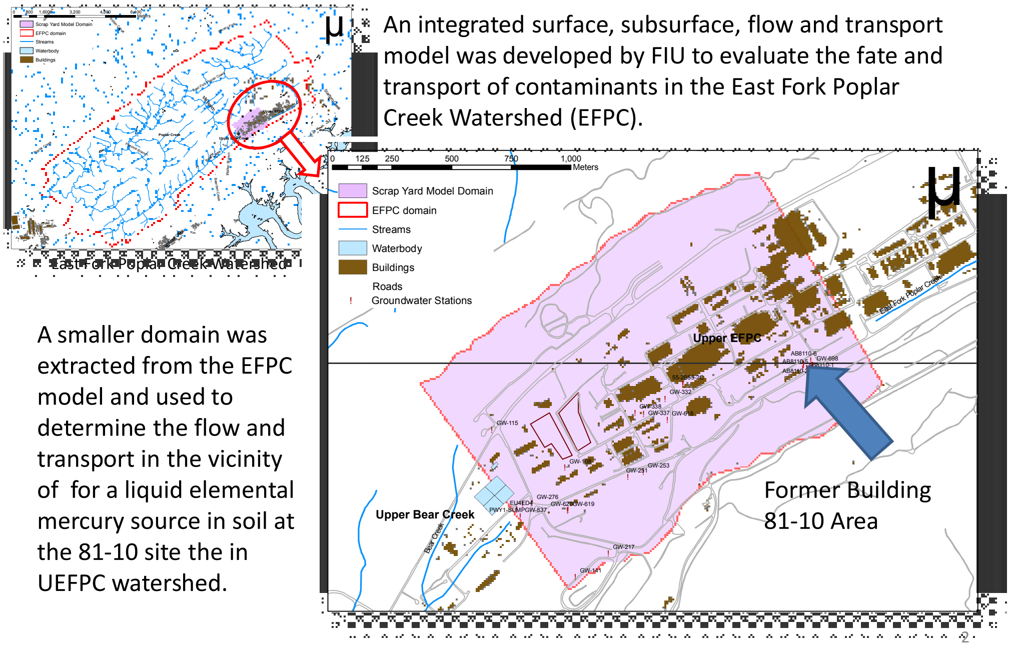


Fig. 8. Telescopically Refined Domain for Former Building 81-10 Submodel

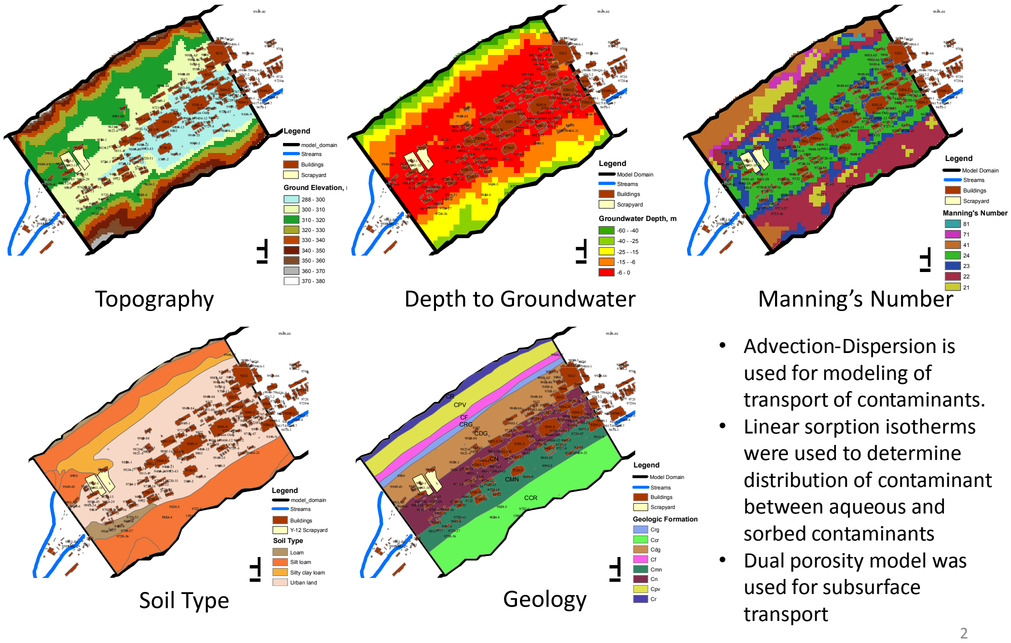


Fig. 9. Spatial Input for Former Building 81-10 Submodel

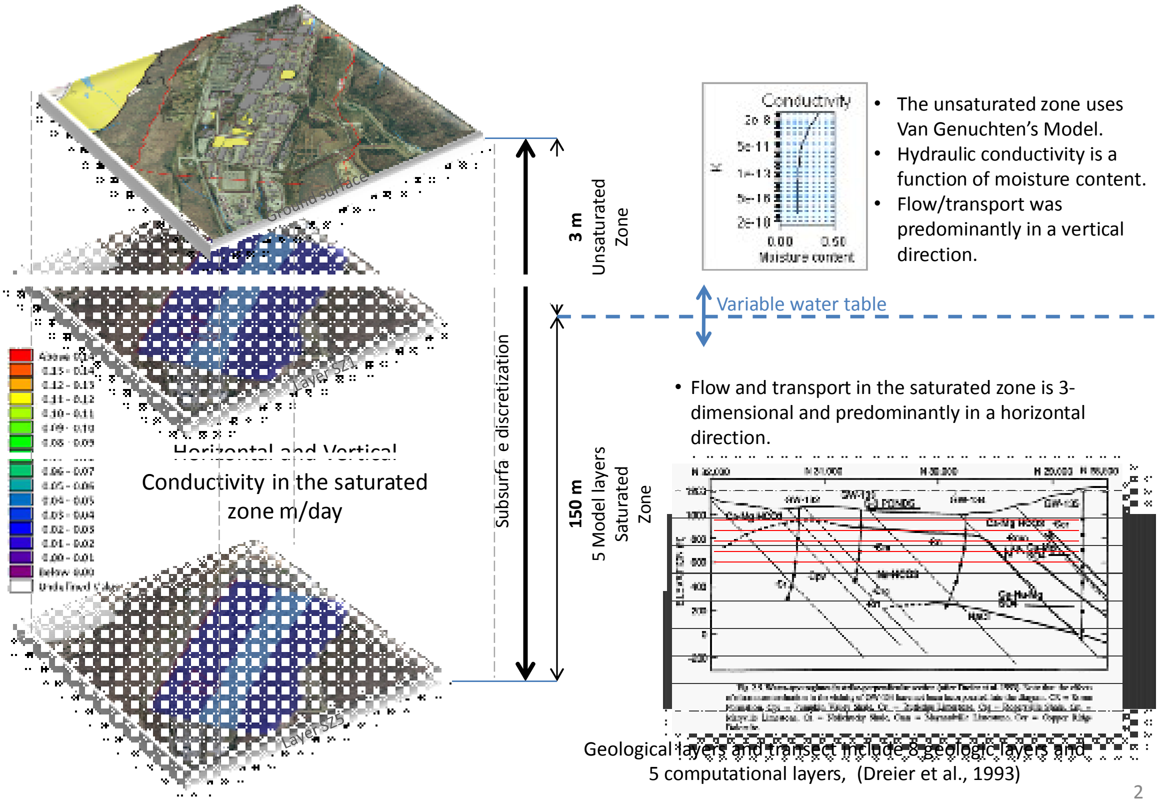


Fig. 10. Subsurface Hydrology in Former Building 81-10 Submodel

For groundwater transport modeling, total mercury concentration is speciated as reactive mercury (HgII) with a high distribution coefficient 1.8 X 10^3 liters/kilogram (L/kg) in soil and unconsolidated materials. Mercury sources input to the sub model are shown on Fig. 4. The sources included unsaturated and saturated soils with variable sorbed concentrations and liquid element mercury leaching at its solubility limit of 60 parts per billion (ppb). The migration of elemental mercury in soil was not modeled as it occurred as a Dense Non-Aqueous Phase Liquid and is held in clay soil near sources of deposition by porosimetry.

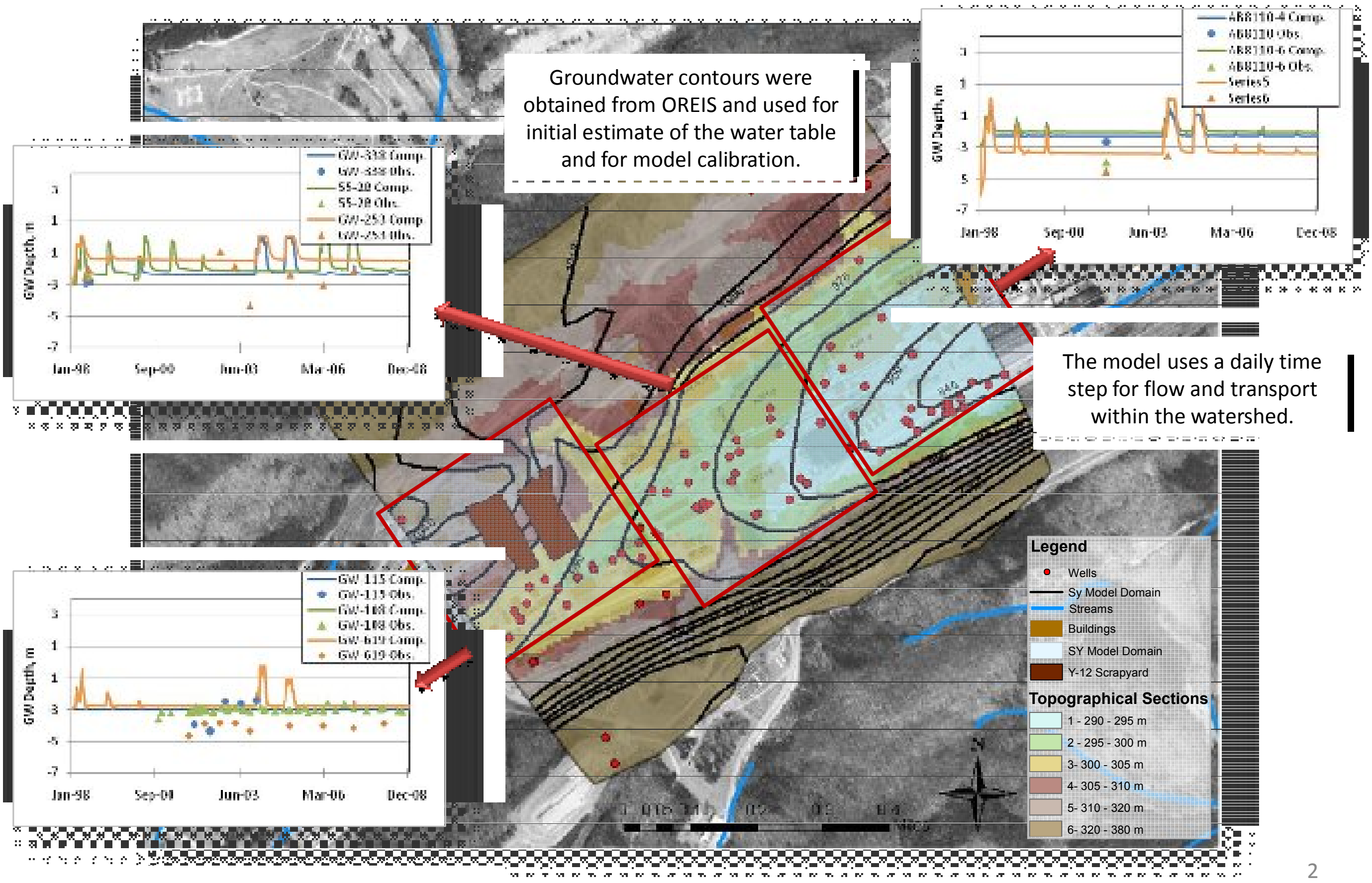


Fig. 11. Head Calibration for 81-10 Subdomain Model

MODELING RESULTS

Modeling on a watershed scale indicated that only removal of contaminated soil and sediment in the vicinity of UEFPC would have any effect on mercury flux in surface water at Station 17 (source B-01 on Fig. 13). Successive removal of other mercury sources in soil farther from the creek would have no effect on surface water flux as shown by three blue green and purple lines that overlie each other represented by source areas B-02, B-03 and B-04. Colloidal transport contributed more than 85 percent of the total mercury flux leaving the UEFPC watershed. High flow conditions increased the shear stress on highly contaminated streambed sediments and resuspended mercury-laden fine particulates as colloidal transport [5] (Fig. 14). This caused most of the mercury flux under high flow conditions.

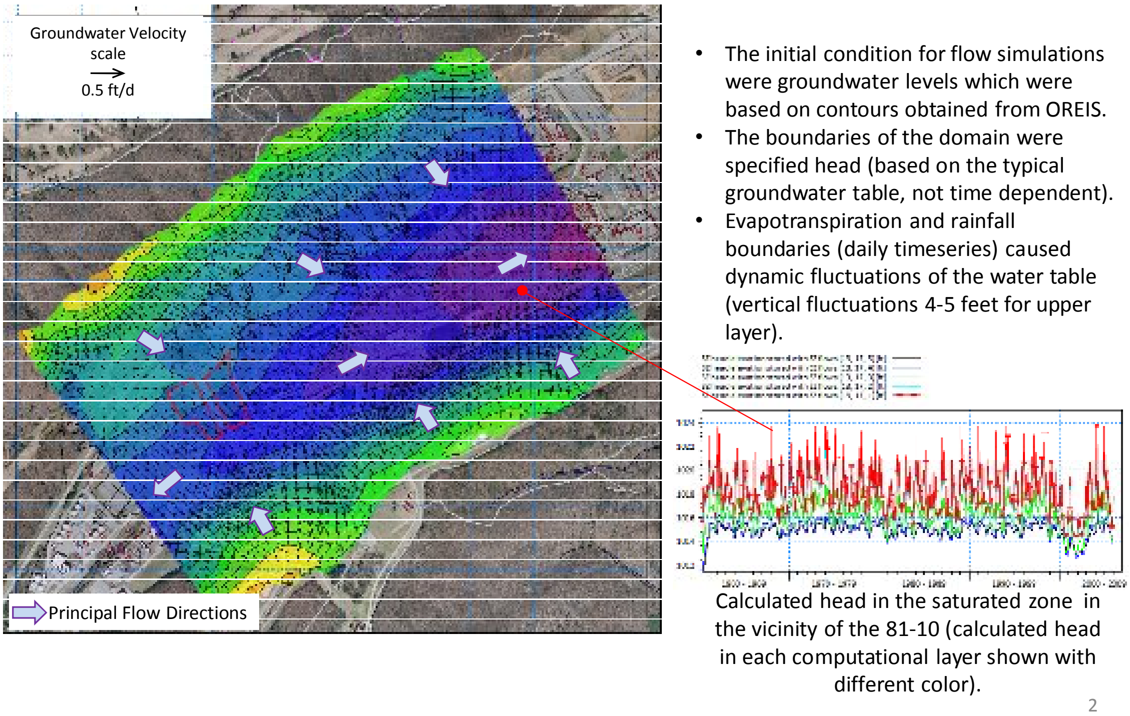


Fig. 12. Groundwater Table and Flow Directions

Simulation of dissolved mercury transport from liquid elemental mercury sources in soil at the former Building 81-10 area indicated that dissolved concentrations would be orders of magnitude below a target industrial groundwater concentration of 0.036 mg/L beneath the source (Fig. 14) and no mercury plume above risk levels would develop. Low concentrations of mercury (defined by 10^{-6} mg/L) reached a steady state distribution in ground water 50 meters downgradient of the source within 50 years. No plumes of dissolved mercury above industrial risk standards would occur where effective porous media conditions are present and source concentrations would not influence concentrations in surface water at Station 17 (Fig. 15).

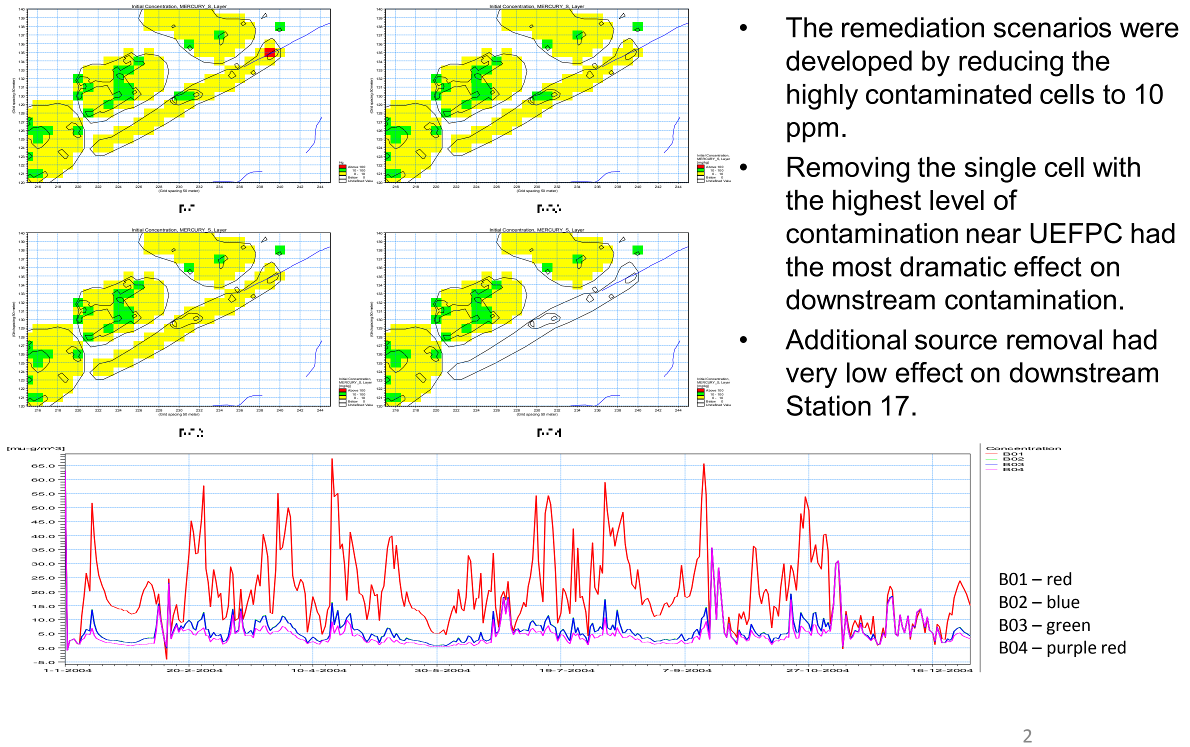


Fig. 13. Effect of Liquid Elemental Mercury Removal/Source Isolation Using Watershed Model

UNCERTAINTY

Because the modeling results are dependent on the retardation factor for reactive mercury and solubility of mercury, some sensitivity analysis should be performed on these parameters. The proposed retardation factor, although conservative, can be influenced by colloidal transport or complexation with ligands in the groundwater system. In addition, the solubility of the mercury (60 ppb) was used as a limiting factor for dissolution of reactive mercury from liquid elemental mercury, however this is valid for only a pure system. In the actual groundwater system this limit is a function of the organic content of groundwater and presence of strong ligands which have high affinity to mercury.

The modeling investigated only transport through shallow groundwater pathways under porous media conditions for sources in soil. It should be recognized that site characterization has indicated that the area under the UEFPC is underlain by the Maynardville Limestone that contains karst conduits. Mercury sources within the limestone and transport to UEFPC may also contribute to total mercury flux at Station 17.

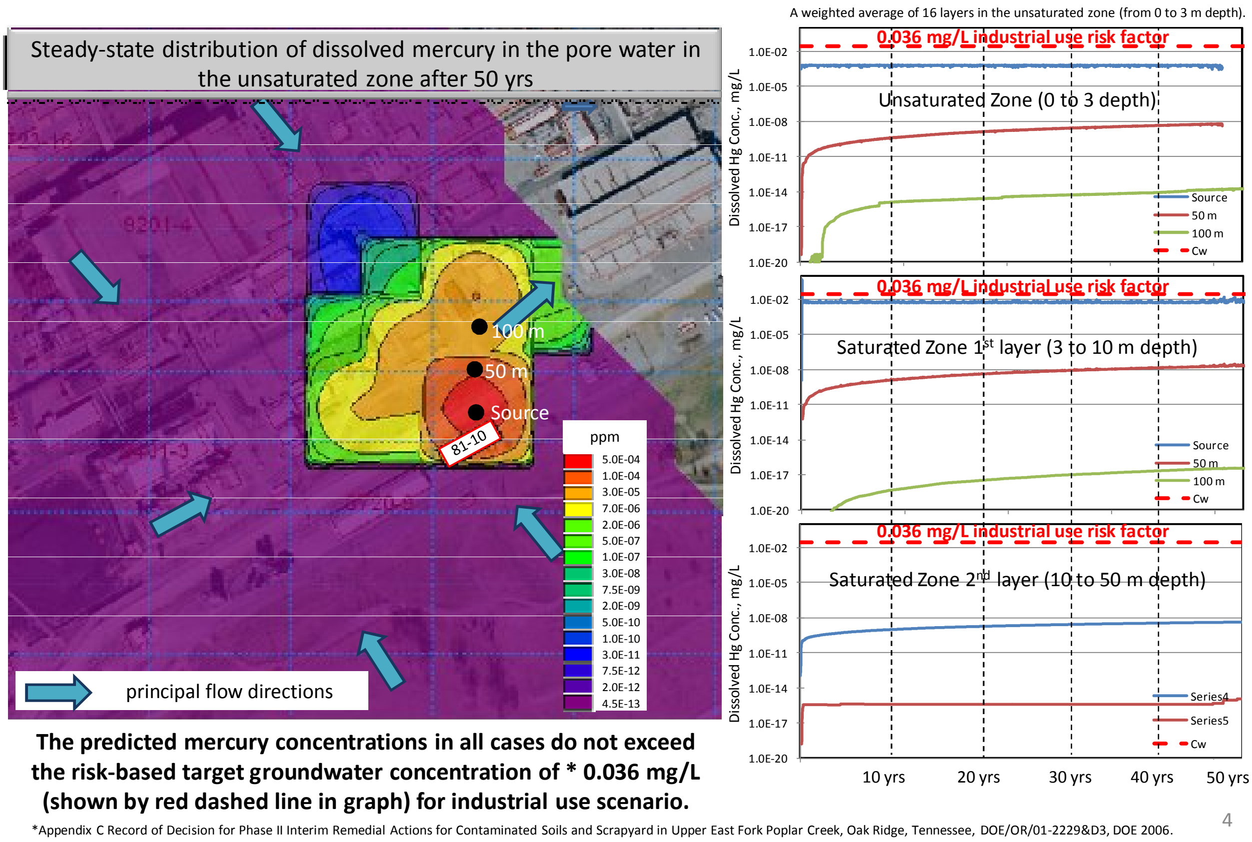


Fig. 14. Predicted Aqueous Mercury Concentrations in 81-10 Domain Model

CONCLUSIONS

Watershed Scale Modeling

- The major mode of mercury transport within the watershed is through mobilization by surface water. Colloidal transport contributed more than 85% of the total mercury flux leaving the Upper East Fork Poplar Creek watershed. This may cause most of the mercury flux under high flow conditions [5, 6].

- Mercury in the soil and sediment source areas adjacent to the stream and in sediment that is eroding can contributed to the flux of mercury at Station 17. Because colloidally adsorbed mercury could be transported in surface water, actions that trap colloids and or hydrologically isolate surface water runoff from source areas would reduce the flux of mercury at Station 17.

Modeling of Transport from a Liquid Elemental Source of Mercury in Soil near Former Building 81-10 with the Submodel

- The low solubility of mercury and high retardation factor in the soil near the former Building 81-10 minimize transport of mercury from soil to ground water. Simulations with a submodel extracted from the watershed model predict that low concentrations of mercury (defined by 10^{-6} mg/L) reached a steady state distribution in ground water 50 meters downgradient of the source within 50 years. However, concentrations in groundwater were below industrial risk levels (0.036 mg/L) by several orders of magnitude. Because the presence of humic acids and other strong ligands can modify the equilibrium concentration of mercury in groundwater and increase transport through groundwater pathways, additional research and modeling is needed to address this uncertainty.

- Simulations of mercury contamination in soil didn't create groundwater plumes above industrial risk standards where effective porous media conditions were present and would not influence concentrations in surface water at Station 17.

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