MODELING TOOLS USED FOR MERCURY TMDLS IN GEORGIA RIVERS

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Abstract. Total maximum daily loads (TMDLs) were developed for mercury in six south Georgia rivers and the Savannah River. Mercury is introduced to these rivers by atmospheric deposition, watershed runoff, and small point source loadings. To produce mercury TMDLs in these rivers, the GIS-based Watershed Characterization System (WCS) and a mercury delivery spreadsheet were developed and applied with the water pollutant fate model WASP5. Together, these models calculate mercury buildup in watershed soils, loading and delivery through the watershed tributary system, and mercury fate in the main stem rivers. These models were applied to six south Georgia rivers and checked against survey data gathered during drought conditions in June, 2000. Despite environmental variability and scientific uncertainties, calculated mercury concentrations in soils, sediment, and water compared reasonably well with the observed data. Example calculations from the Upper Ochlockonee River are given here.

INTRODUCTION

The Clean Water Act and associated regulations require each State to identify waters not meeting water quality standards applicable to their designated uses. Total maximum daily loads (TMDLs) are required for pollutants violating these standards. The Consent Decree in the Georgia TMDL lawsuit required that TMDLs for mercury in six south Georgia rivers be proposed by August 2000. These include the Ochlockonee, the Suwanee, the Withlacoochie, the Alapaha, the Satilla, and the St. Mary's rivers. In addition, mercury TMDL proposals for the middle and lower Savannah River were required by December, 2000. The proposed mercury TMDLs for these rivers are posted on EPA's web site (U.S. EPA, 2000a).

METHODS

Three separate software tools were used to produce the mercury TMDLs – the Watershed Characterization System (WCS), a mercury delivery spreadsheet, and the water pollutant fate model WASP5. The WCS takes wet and dry atmospheric deposition and calculates mercury concentrations in soil as well as reduction and volatilization loss, leaching, and runoff and erosion fluxes to the stream system. The mercury delivery spreadsheet calculates the fraction of mercury from the landscape that is lost in the watershed's tributary system due to reduction and volatilization. Speciation of the watershed loadings between divalent and methyl mercury is based on site-specific data. WASP5 takes the speciated loadings delivered from the watershed and from point sources, and calculates total and methyl mercury concentrations in the water column and sediments of the river. Processes simulated include advection, sediment exchange, reduction, volatilization, methylation, and demethylation in the water column, and methylation and demethylation in the sediments.

The WCS Mercury Extension

The WCS is a GIS model recently-developed by U.S. EPA Region IV and Tetra Tech for calculating sediment and contaminant fate in watersheds (US EPA, 2000b). The hydrology calculation for pervious grids is based on the Soil Conservation Service Curve Number approach (Ogrosky and Mockus, 1964). The sediment yield calculation for pervious grids is based on the modified Universal Soil Loss Equation, MUSLE (Williams, 1975). For impervious and water surface areas, rainfall is routed directly to the tributary network. Grid resolution is 40 by 40 meters.

The mercury extension developed for this project is derived from IEM-2M, the U.S. EPA mercury fate spreadsheet documented in the Mercury Report to Congress (U.S. EPA, 1997). The IEM-2M was based on simpler, long-term average hydrology and sediment yield equations, but simulated three mercury components – elemental mercury, Hg^0, inorganic divalent mercury, Hg(II), and monomethyl mercury, MeHg. Because atmospheric mercury deposition is primarily Hg(II), and because concentrations of Hg^0 and MeHg are much less than Hg(II) in soil, soil mercury is treated here as a single total mercury component. Sunlight and microbial reduction in the surface layer reduce the Hg(II) to Hg^0, which is volatile and quickly returned to the atmosphere.

Reduction of Hg(II) is much slower than volatilization of Hg^0, and so this 2-step loss process can be represented as a single step controlled by the reduction rate constant. Following the IEM-2M application, this surficial reduction loss constant is normalized by soil moisture and the surficial layer depth. The normalized rate constant was set to 0.0005 L/L_w-day over a 5 mm layer, following observations presented in Carpi and Lindberg (1997) as reported in U.S. EPA (1997).

To simulate mercury in a watershed over a specified period of years, initial background soil mercury concentrations are specified, along with wet and dry atmospheric mercury deposition fluxes. The WCS mercury module calculates surficial soil mercury concentrations over time using a mass balance on pervious watershed grids. Mercury in the soil partitions between dissolved phase in the soil water and particulate mercury on the soil solids. Dissolved mercury is lost from the surficial soil layers through percolation and runoff. Particulate mercury is lost through erosion. A fraction of the soil mercury is reduced and volatilized back to the atmosphere. Runoff and erosion loadings of mercury from the soil are delivered to the watershed tributary system. Percolation carries an insignificant loading of mercury to the shallow groundwater due to the high sorption to soil solids. For impervious areas of the watershed, atmospheric mercury deposition is delivered to the tributary system without loss. Similarly, direct atmospheric deposition to tributary water surface areas is provided.

The Mercury Delivery Spreadsheet

Mercury loadings to the tributary network must be delivered to the main stem of the rivers where TMDLs are calculated. The only loss mechanism considered in the tributary network is the reduction of Hg(II) in water followed by volatilization of the resulting Hg^0. The first step is to calculate the maximum travel time τ_{max} through the tributary network for a given flow condition. Velocity was calculated from flow using hydraulic geometry coefficients, and τ_{max} was calculated from the total tributary length divided by the average velocity. Assuming first-order loss kinetics, the mercury load from a given watershed grid will be reduced by a factor of $exp(-k_r \cdot \tau)$, where k_r is the loss rate constant in day^{-1} and τ is the travel time in days. Integrating this factor from τ of 0 to τ_{max} gives an average delivery ratio through the tributary network:

$$delivery\ ratio = (1 - e^{-k_r \cdot \tau_{max}}) / k \cdot \tau$$

For the simulations in all South Georgia watersheds, the reduction loss rate constant served as a calibration parameter that was constrained within reported range of 0.005 to 0.2 day^{-1}. Tributary loads were divided between HgII and MeHg based on observed data. No attempt is made to predict the speciation of loadings.

The WASP5 Mercury Model

WASP5 (Ambrose, et al., 1987) was chosen to simulate mercury fate in the Ochlockonee River. WASP5 is a general dynamic mass balance framework for modeling contaminant fate and transport in surface waters and the underlying sediments. The mainstem of the Ochlockonee River was divided into 6 reaches. Each reach was further divided into 2 vertical compartments representing surface water and surficial sediment. The 2 cm deep surficial sediment layer actively exchanges silt and clay-sized solids as well as mercury with the water column. In addition, this layer is the site for active microbial transformation reactions. Sediment-water column diffusion coefficients were set at 10^{-5} cm^2/sec.

Two solids classes were simulated – sand and silt. Sand makes up most of the benthic sediment compartments, which have a dry bulk density of 0.5 g/mL and porosity of 0.8. Silt is found both suspended in the water column and in the sediment. These simulations assumed that 10 mg/L of silt enters the mainstem from the subwatersheds, settling out at a velocity of 0.3 m/day. Silt in the surficial sediment compartments is assumed to resuspend at a velocity of 0.006 m/day, leading to a concentration of about 1% fines in the surficial sediment. The exchanging silt carries sorbed mercury between the water column and surficial sediment.

Mercury was simulated as 3 components – elemental mercury, Hg^0, inorganic divalent mercury, Hg(II), and monomethyl mercury, MeHg. Hg(II) and MeHg partition to solids and to dissolved organic carbon (DOC). These are represented as equilibrium reactions governed by specified partition coefficients. The three mercury components are also subject to several transformation reactions, including oxidation of Hg^0 in the water column, reduction and methylation of Hg(II) in the water column and sediment layer, and demethylation of MeHg in the water column and sediment layer. These are represented as first-order reactions governed by specified rate constants. Reduction and demethylation are driven by sunlight, and the specified surface rate constants are averaged through the water column assuming a light extinction coefficient (here, 0.5 m^{-1}). In addition to these transformations, Hg^0 is subject to volatile loss from the water column. This reaction is governed by a transfer rate calculated from velocity and depth, and by Henry's

Law constant, which was set to 7.1×10^{-3} L-atm/mole-K. Under average flow conditions, velocity ranges from 0.2 to 0.3 m/sec, while depth ranges from 0.37 to 0.69 m.

Simulation Procedures

The Ochlockonee Watershed was subdivided into 11 subwatersheds, and the WCS was run for 30 years with wet and dry atmospheric deposition fluxes of 12 and 6 $\mu g/m^2$-yr, respectively. Soil mercury concentrations rose from a specified background level of 20 μg/g to new equilibrium levels. Average loadings to the tributary system by pervious and impervious runoff, erosion, and direct deposition were accumulated for each subwatershed.

Mercury delivery ratios through the subwatershed tributary systems were calculated for drought and average flow conditions. The delivery ratios were calibrated by varying the reduction rate constant and comparing delivered total mercury concentrations with instream concentrations measured during an extreme drought in June 2000. No attempt was made to vary this rate constant by subwatershed to match instream mercury gradients more precisely. This rate constant was used along with average hydraulic conditions to calculate average delivery ratios for use in the TMDL calculations.

Two separate simulations of mercury in the Ochlockonee River were run representing average flow and drought flow conditions. The average flow simulation was run for 20 years to achieve steady-state conditions. Drought flow conditions were then run for 180 days using the average-flow concentrations as initial conditions. Total watershed loadings and average flow delivery ratios were used to calculate expected average mercury concentrations. Direct dry deposition loadings to water surfaces were used with drought delivery ratios to give estimated tributary loadings to the Ochlockonee River during late spring and early summer 2000. Volumes, depths, and velocities were adjusted from average flow values to drought flow values using hydraulic geometric relationships. Model parameter values are detailed in U.S. EPA (2000a).

RESULTS AND DISCUSSION

The WCS model gives soil mercury concentrations by subwatershed grid and loadings for several pathways. As summarized in Table 1, predicted soil concentrations compare well with the two soil mercury samples, with the median relative error of -3 %. Calculated loadings from the subwatersheds to their tributaries ranged from 0.7 to 1.1 $\mu g/m^2$-yr, representing more than a 90% reduction from atmospheric deposition. The total mercury loading from all subwatersheds came to 3.8 kg/yr, 39% attributed to erosion, 28% to impervious runoff, 22% to pervious runoff, and 11% to direct deposition. Point source loadings from the 10 permitted facilities were comparatively small (less than 0.01%).

Mercury delivery ratios through the subwatershed tributaries were calculated for average and drought conditions using a calibrated reduction rate constant of 0.05 day^{-1}. Based on estimated average travel times of 7 to 17 days, average reduction factors ranged from 0.73 to 0.88. During drought conditions, travel times were estimated to be 42 to 330 days, causing reduction factors from 0.08 to 0.48.

WASP5 calculations of mercury concentrations under drought conditions are summarized in Table 1. Median calculated concentrations compared reasonably well with observed data, with relative errors for various mercury components of ±20%. No attempt was made to fine-tune the model predictions by adjusting model parameters spatially. Sensitivity analyses revealed that in-stream concentrations are not strongly affected by changes in process rate constants assigned to the river or its sediments. The travel time along the main stem is short relative to the process half-lives. This implies that MeHg fractions in the Ochlockonee River are determined by methylation and demethylation in the wetlands and tributaries feeding the river.

Results of the average flow simulation are summarized in Table 2. Using the full set of loading pathways and the higher delivery ratios, the total loadings for this simulation were from 50 to 500 times that for the drought simulation. The average flows were about 100 times the drought flows. The resulting total mercury concentrations are about 2 to 4 times higher than the drought flow concentrations. The maximum predicted concentration in the water column of 5.86 ng/L occurs in the third reach. To bring this concentration down to the in-stream target of 0.65 ng/L, an 89% reduction of the total mercury loading is needed.

CONCLUSIONS

Several factors complicate the characterization of mercury behavior in individual rivers, including measurement uncertainty in mercury loadings, environmental variability over a watershed, and scientific uncertainty in mercury process kinetics. Modeling alone cannot predict mercury concentrations and speciation required for a TMDL. Survey data must be gathered, including mercury concentrations in soil, sediment, and

Table 1. Summary of observed and calculated concentrations in Ochlockonee River for drought flow conditions

	Observed Values	Calculated Range	Observed Median	Calculated Median	Relative Error
Total Hg, soil, ng/g	74, 79	63-85	76.5	74	- 3%
Total Hg, sediment, ng/g	3.5, 8.5	4.5 - 6.9	6.0	5.2	-13%
Total Hg, water, ng/L	1.4, 1.6	0.9 - 2.3	1.5	1.8	+20%
MeHg, sediment, ng/g	0.04, 0.10	0.07 - 0.11	0.072	0.085	+18%
MeHg, water, ng/L	0.21, 0.25	0.07 - 0.22	0.23	0.17	-22%

Table 2. Predicted mercury concentrations in Ochlockonee River under average loading and flow conditions

River Reach	1	2	3	4	5	6
Total Hg, water, ng/L	3.8	5.3	5.9	4.6	4.4	4.0
Total Hg, sediment, ng/g	247	347	383	302	282	259
MeHg, water, ng/L	0.54	0.75	0.82	0.65	0.61	0.56
Hg^0, water, ng/L	0.04	0.04	0.05	0.05	0.07	0.09

water. In particular, data should be taken within tributaries as well as within the main river.

Despite the difficulties, results of the drought flow simulation offer some degree of confidence in the models' joint ability to relate atmospheric deposition to river mercury concentrations. Little calibration was required to approximate the median concentrations. More data and model definition would be necessary to characterize and match spatial and temporal trends. Future model development should include more detailed transport and reactivity within the tributary system, including methylation and demethylation, storage in stream sediments, and burial loss in ponds and wetlands.

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